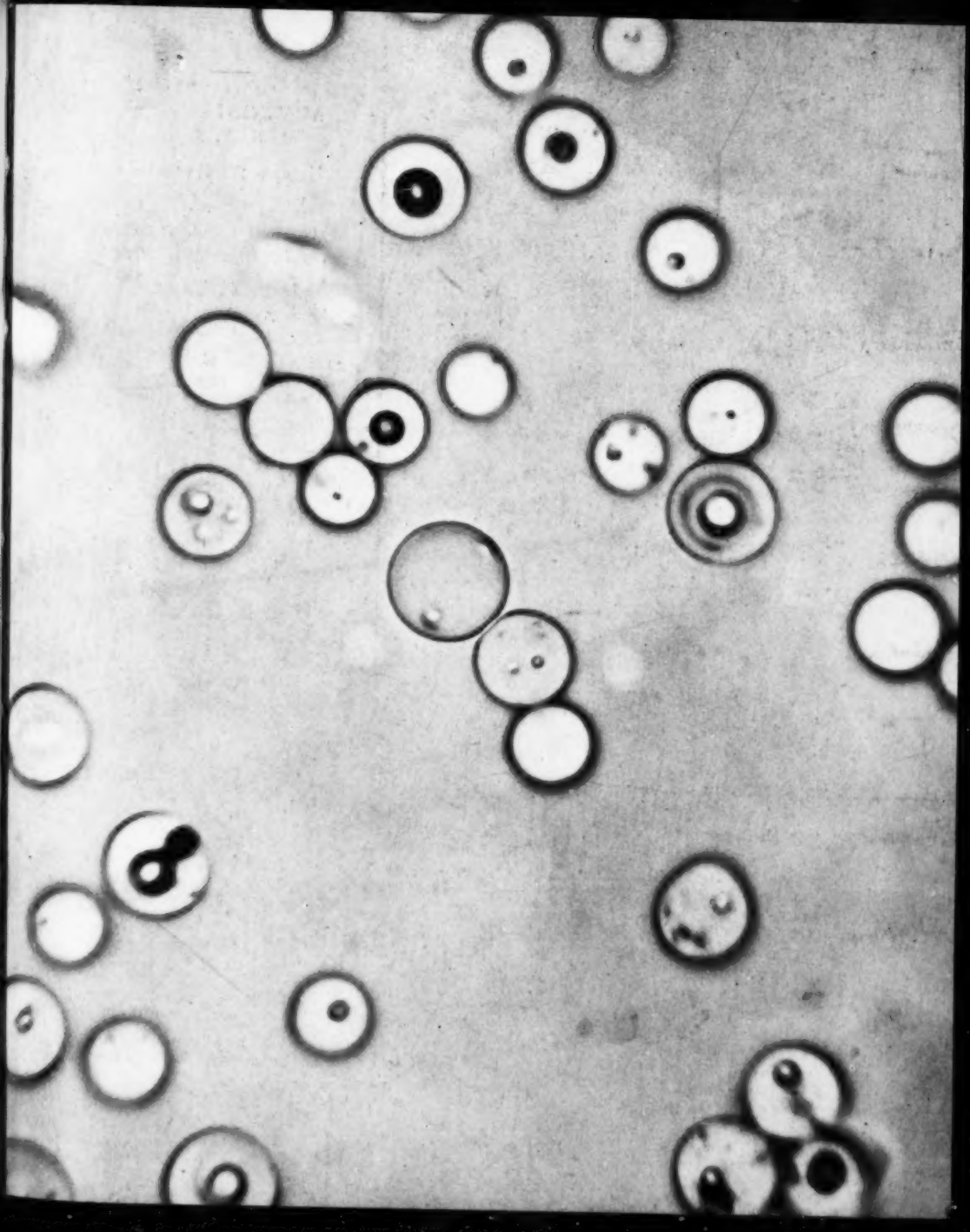
JOURNAL OF APPLIED PHYSICS



JOURNAL
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OCTOBER, 1942 Vol. 13, No. 10

In This Issue

Page

In This Issue

Physics of Pigments and Glasses. A Conference Held at The University of Pennsylvania F. SEITZ 595

Basic Principles Involved in the Preparation of Pigments ROSCOE H. SAWYER 596

Basic Principles Involved in the Glassy State B. E. WARREN 602

Physics of Pigments in Dispersed Systems HENRY GREEN 611

Mechanical Properties of Glass F. W. PRESTON 623

Glass-Pigment Systems C. ROBERTSON 635

Darkening of Materials by Light FREDERICK SEITZ 639

Contributed Original Research

Rate of Crystal Growth in Drawn Tungsten Wires as a Function of Temperature C. S. ROBINSON, JR. 647

Vibration Characteristics of Nearly-Complete, "Free-Free" Circular Rings F. P. BUNDY AND C. W. BANKES 652

In Every Issue

New Books 644

Here and There 646

Calendar of Meetings 622

Index to Advertisers xii

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Volume 13 October, 1942 Number 10

Physics of Pigments and Glasses

A Conference Held at the University of Pennsylvania

ALTHOUGH pigments and glasses may at first sight appear to have little in common, there are actually a number of physical and chemical properties that are of interest for both materials. For example, both play a role in the formation of ceramics and enamels; both have interesting mechanical properties that appear when they are ground or when their mechanical strength is under consideration; problems of opacity and light scattering arise when pigments are used in paints or when glasses are used in opal or ruby form; both may be darkened or decomposed by the action of visible or ultraviolet light. In view of this fact, it was decided that the second of the conferences on applied physics held at the University of Pennsylvania could profitably be devoted to the properties of pigments and glasses. This conference was sponsored jointly by the Physics Department of the University of Pennsylvania and by the Philadelphia Chapter of the American Society for Testing Materials. The meetings were held on the afternoon and evening of Friday, May 15th, and on the morning of Saturday, May 16th.

As might be expected, the pressure of war activities made it difficult to obtain speakers on all of the topics originally planned; however, many of the leading investigators in the fields were willing to add to already burdened schedules and thereby guaranteed the success of the meeting.

The program of speakers and their topics follows:

MR. R. H. SAWYER, *Krebs Pigment and Color Corporation, Baltimore, Maryland,* **The Basic Principles Involved in the Preparation of Pigments**

PROFESSOR B. E. WARREN, *Massachusetts Institute of Technology, Cambridge, Massachusetts,* **The Basic Principles Involved in the Glassy State**

DR. R. B. BARNES, *American Cyanamid Company, Stamford, Connecticut,* **The Electron Microscope and the Determination of Particle Size**

MR. H. GREEN, *The Interchemical Corporation, New York, New York,* **The Physics of Pigments in Dispersed Systems**

DR. F. W. PRESTON, *The Preston Laboratories, Butler, Pennsylvania,* **The Mechanical Properties of Glasses**

DR. C. ROBERTSON, *R. & H. Division, E. I. du Pont de Nemours and Company, Perth Amboy, New Jersey,* **Glass—Pigment Systems**

PROFESSOR F. SEITZ, *Randal Morgan Laboratory of Physics, University of Pennsylvania, Philadelphia, Pennsylvania,* **Deterioration of Materials by Light**

It may be added that the chairmen of the various sessions were responsible for extensive and stimulating discussion. These were: PROFESSOR G. P. HARNWELL, University of Pennsylvania; DR. E. R. ALLEN, Krebs Pigment Company; DR. J. T. LITTLETON, Corning Glass Works; DR. C. GROVE, United Pigment and Color Company; PROFESSOR E. C. BINGHAM, Lafayette College; MR. F. C. FLINT, Hazel-Atlas Glass Company; and DR. J. E. BAILEY, Plax Corporation, Hartford, Connecticut.

F. Seitz

The Basic Principles Involved in the Preparation of Pigments

BY ROSCOE H. SAWYER

Krebs Pigment and Color Corporation, Curtis Bay, Baltimore, Maryland

A PIGMENT is defined simply as "a coloring material." A more precise definition is given by Thorpe,[1] "Insoluble, colored powders yielding paints when admixed with suitable media. This definition excludes dyes or stains which are soluble in the vehicles used." Pigments provide the color, opacity, and light diffusing properties of most surface coatings and of many other articles of commerce. Industrially pigments are classified as whites or colors. Compositions containing white pigments only reflect and diffuse substantially all incident light. Colors have highly selective spectral reflection curves.

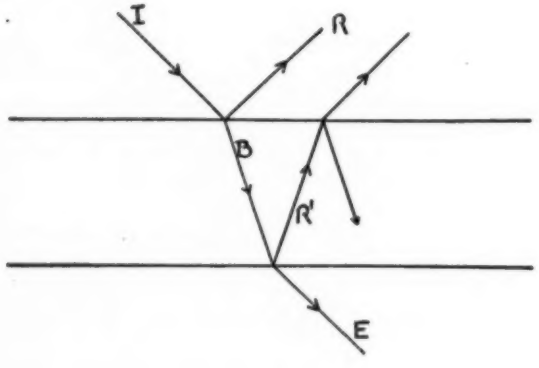

FIG. 1.

The optical properties — color, brightness, opacity, and light diffusion — are paramount in the preparation of pigments and in a large fraction of their usage. These properties derive simply from the refractive index and light absorption properties of the pigment material and from the particle size in which the material is supplied. The basic relations are well known.

Figure 1 shows typical phenomena in the passage of light through two different media. Light I passes from a medium of lower to a medium of higher refractive index. At the interface light is refracted, B. A portion is reflected, R. The angle of reflection is equal to the angle of incidence. At the second interface light passes from the medium of higher into the medium of lower refractive index with a similar refracted emergent beam E and reflected R'. Throughout the length of each light path absorption also occurs. Well-known laws govern each of these processes.

The amount of light reflected at the interface is governed by refractive indices as shown by the Fresnel equation (normal incidence)

$$R=\left(\frac{n_2-n_1}{n_2+n_1}\right)^2,$$

where n_1 and n_2 are refractive indices of the two media. Figure 2 shows this relation graphically. Suitable media for paints and other pigmented compositions range upwards from 1 to about 1.5 in refractive index. It should be noted that, even with extremely large refractive index, only a small portion of light is reflected.

Fresnel reflection is almost entirely responsible for reflection of light from gross non-metallic surfaces. Since but a small portion of the light is reflected from a single interface, a considerable number of interfaces are required to reflect substantially all light. Parallel layers of high and low refractive index materials accomplish this without diffusing the reflected light (Fig. 3). A massive material, immersed in a continuous medium of different refractive index, reflects a progressively larger fraction of the light as it is broken down to smaller fragments (Figs. 4 and 5). Such reflected light is well diffused.

Regular reflection ceases to follow this law when particle size approaches the wave-length of light. For fine sizes light is scattered. Rayleigh[2] investigated scattering extensively, particularly in the region of size considerably smaller than the wave-length of light. The Rayleigh equation

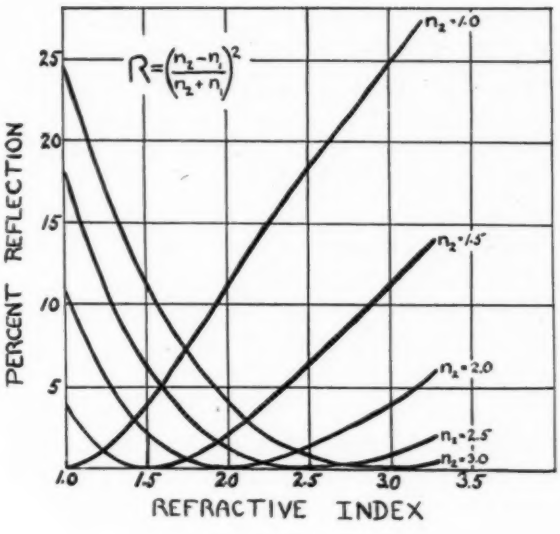

FIG. 2.

is quite complicated:

$$I \propto I^0 \frac{(D'-D)^2}{D^2}(1+\cos^2\beta)\frac{m\pi T^2}{\lambda^4},$$

where

I^0 = intensity of incident light,
I = intensity of light scattered in direction making angle β with the incident beam,
D' = optical density of particle (proportional to refractive index squared),
D = optical density of medium,
m = number of particles/unit volume,
T = volume of particle,
λ = wave-length of scattered light.

This equation ceases to be correct for particle sizes close to the wave-length of light. It will be noted that, in the region of scattering, light scattered increases as particle size increases (Fig. 6).

Thus, we see that (Fig. 7), for particles finer than the wave-length of light, *scattering* increases as particle size increases, while for particles coarser than this, *reflection* increases as particle size decreases. Around the wave-length of light there should be an optimum.

The relation between optical properties and particle size has been investigated by many workers. Theoretical treatments have been published by Mie,[3] Shoulejkin,[4] Ryde,[5] and others.

Clewell[6] calls attention to a third mechanism by which a particle scatters or reflects light falling on it—diffraction scattering. When light falls upon a small particle, the light is diffracted into a cone. According to Clewell, this diffraction should be a maximum when the apex angle of the cone is 180°. By diffraction theory

$$\sin\theta = 0.61\lambda/n_0 d,$$

where

θ = half apex angle of the diffracted cone,
n_0 = refractive index of vehicle,
d = diameter of particle.

Therefore, maximum diffraction scattering occurs when $\theta=\pi/2$, or

$$d=\frac{n_0\lambda}{0.61}.$$

Clewell developed the following equation:

$$S \propto \frac{[(n^2-1)/(n^2+2)]^2}{d[(0.61\lambda/n_0 d)^2-1]^2 + \lambda^2/\{n_0^2 da[(n-1)^2+1/a]\}},$$

where

S = scattering,
n = refractive index of particle relative to medium,

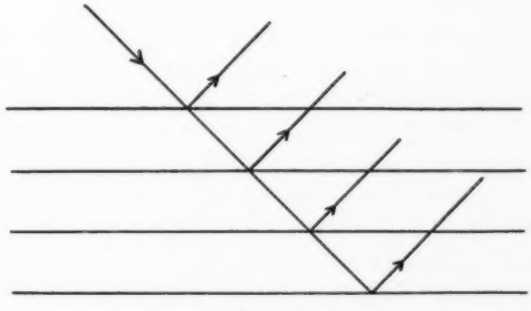

FIG. 3.

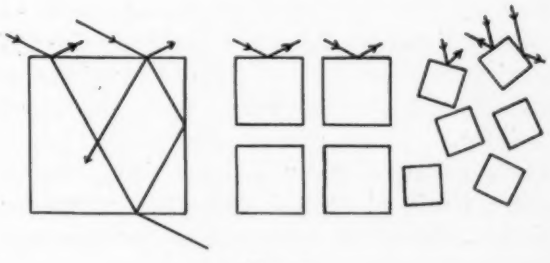

FIG. 4.

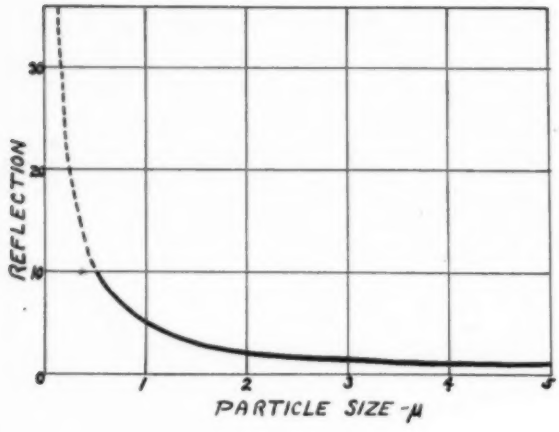

FIG. 5.

n_0 = refractive index of medium,
d = diameter of particle,
a is a constant.

Although this equation is somewhat empirical, it does reduce to the proper forms for Rayleigh scattering and Fresnel reflection and shows an optimum particle size for scattering which varies with wave-length.

Figure 8 shows scattering as a function of particle size for different wave-lengths using Clewell's equation. Pronounced optima in scattering are shown. The optima are at progressively finer size as wave-length decreases. The precise location of these optima experimentally is not easy.

Stutz and Pfund[7] demonstrated such an optimum for ZnO at 0.24μ. This is slightly less than the wave-length in this material of the light used. Their measurements of particle size were based upon microscope measurements using direct photomicrographs for coarser particles and ultramicroscopic counts for finer particles. More recent work has thrown considerable doubt on the absolute value of particle size measurements in this critical size range.[8–11]

Bailey, Nichols, and Kraemer[12] made measurements of Nujol emulsions in water solutions of glycerine. Similar optimum light absorption was found. Particle size was measured by the ultracentrifuge.

More information on the relation between particle size and optical properties would be desirable. Perhaps the electron microscope may permit better correlation.

Reflection and scattering are responsible for the light reflecting and diffusing properties of pigments and of pigmented compositions. These two processes do not greatly alter the spectral composition of the incident light. They occur at interfaces between materials of different refractive index. Interfacial efficiency is low. Therefore, light must penetrate through a considerable thickness of material and number of interfaces before the light reflected and diffused by the pigmented composition is not further affected by its thickness.

The passage of light through any medium is accompanied by some absorption. According to Lambert's law the light transmitted through a thickness x of a given medium is

$$I = I_0 e^{-kx},$$

where I_0 is the initial light intensity and k is the absorption coefficient (Fig. 9). Absorption of light by the medium or pigment in a pigmented composition reduces the intensity of light reflected from the composition and may alter the spectral distribution or color of this light.

Thus, we see that a white pigment must be transparent and colorless—that is, must have a low and not particularly selective absorption. Its light reflection and diffusion properties are due to refractive index and particle size.

So long as pigment and pigmented medium have very low absorption, the pigmented composition will be white, even though the difference in refractive index is not large and the particle size only roughly approximates the optimum.

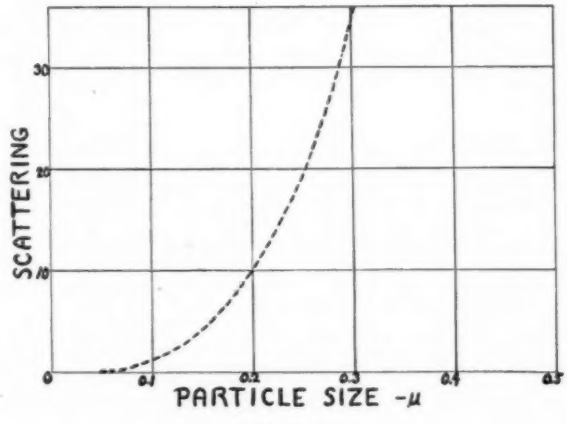

FIG. 6.

The pigmented composition will not have great hiding power or opacity unless the refractive index difference is large and particle size is close to optimum.

In the foregoing, reflection and scattering are considered for the single particle without consideration of mutual effects between particles. For dilute systems it is safe to do this. In practical pigmented systems, however, particles are very close together or even in contact so that particle separations and mutual effects cannot be ignored. It has been demonstrated that pigment efficiency is greatly influenced by pigment concentration.[13, 14]

Not much is known regarding the way in which reflection and scattering at an interface are influenced by proximity of a second interface. Undoubtedly interference effects occur when fine particles are crowded together. Such interference of light within the particle may decrease the effectiveness of the particle as a reflecting unit in the same way that a thin coating on a lens increases its transmission.[15]

In the case of *total* reflection it is known that close proximity of a second interface permits some of the light otherwise totally reflected to pass on through.[16] This results from penetration of the disturbance a few wave-lengths beyond the interface into the material of lower refractive index. Whether close proximity of a second interface influences regular Fresnel reflection is not known.

Much has been written concerning hiding power of pigments and methods of measurement. Discussion of this work is beyond the scope of the present paper. Suffice it to say that the modern white pigments, ZnS, and anatase and rutile TiO_2, with refractive indices from 2.37 to 2.72, have hiding powers many times greater than the earlier ZnO and white lead with refractive indices of 2.02 to 2.06. The recent development of pigment rutile (refractive index 2.72) increases the hiding power value roughly one-third over anatase (refractive index 2.53).[13]

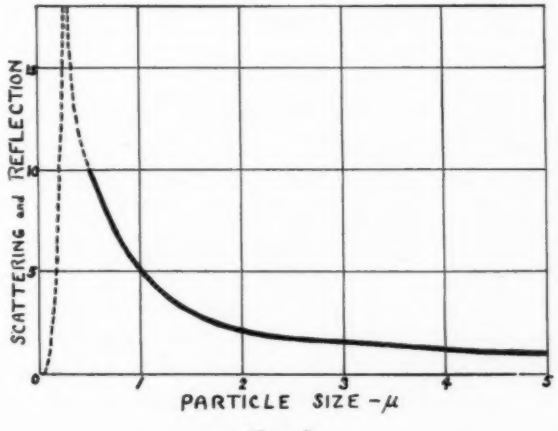

FIG. 7.

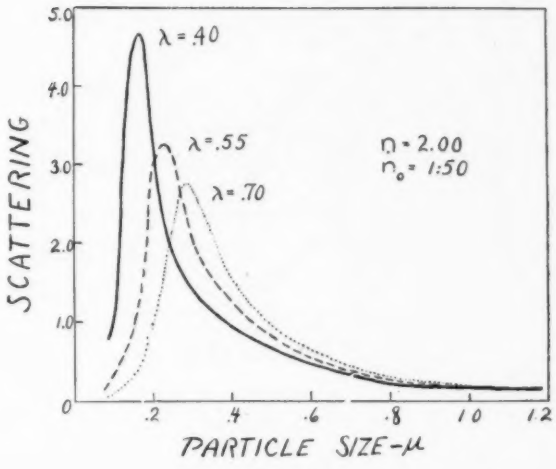

FIG. 8.

At this point some digression should be permitted. It has frequently been observed that paints have higher hiding power in blue than in red light. It has likewise been shown that the tinting of a white paint results in large or small increase in hiding power depending upon the color to which the paint is tinted.[17] These facts follow directly from the principles stated earlier. Scattering varies inversely as the fourth power of the wave-length. Furthermore, the common white pigments have significantly higher refractive indices for blue than for red light (Fig. 10). Since scattering varies as the fourth power of the refractive index and reflection as the square, the scattering-reflecting power of the pigment is much greater to blue than to red light. This greater scattering-reflecting power to blue light makes the pigmented composition look bluish in thin film but has little effect in thick film, since the yellow and red portion of the spectrum merely penetrate somewhat more deeply into the pigmented composition before being completely returned.

When the pigment material is not transparent,

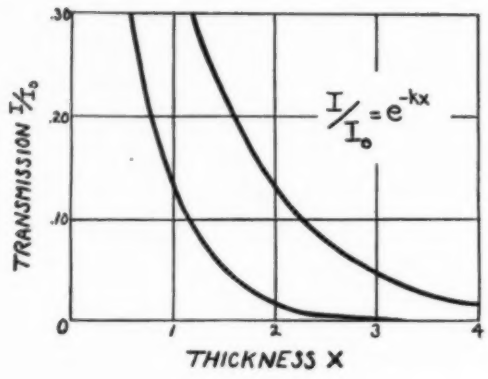

FIG. 9.

absorption competes with reflection-scattering. The light reflected by the pigmented composition is then less than the light falling on the surface. If absorption is selective, the pigmented composition becomes colored. To develop a deep color it is necessary that absorption be intense so that complete absorption of the absorbed wave-lengths takes place in passage through a thin pigment layer. Then almost none of the absorbed wave-lengths is returned from the pigmented composition by interfacial reflection and scattering.

The colored pigment, therefore, has a very high absorption coefficient. Hiding power varies with refractive index and particle size as it does for white pigments. For a given material, that is, fixed refractive index and absorption coefficient, depth of shade varies more or less with particle size. Variation of depth of shade with particle size is great for materials of low absorption and small for materials of high absorption.

From the foregoing it is seen that the manufacture of pigments is to a great degree the preparation of the selected material in the desired particle size range. This is true even though control of the manufacturing operation is usually on the basis of specialized performance tests. Precise, easy measurement of particle size would be desirable. The electron microscope may open the door to this.

The desired particle size range is the same order as the wave-length of light. The usual methods of obtaining this size are: (1) grinding of massive material (earth colors); (2) direct precipitation to desired size, (a) from fume (ZnO), (b) from solution (dry colors—white lead); (3) calcination (ZnS, TiO_2). In the last case the pigment usually is precipitated in fine size and then grown to desired particle size by the calcination process.

Pigments, particularly those prepared by precipitation, are crystalline in structure. When calcination follows the precipitation process, the calcined product is distinctly crystalline to x-rays even though well aggregated. The optical properties are markedly influenced by minor impurities. Thus, a few parts per million of copper, nickel, or chromium, for example, have a very degrading effect on the absorption characteristics of ZnS or TiO_2. Elaborate purification of materials is a necessary part of the preparation of high grade pigments.

The particle size range for optimum optical properties verges on the colloidal. Consequently, surface chemistry plays a large role both in the preparation and use of pigments. This field also is beyond the scope of this paper.

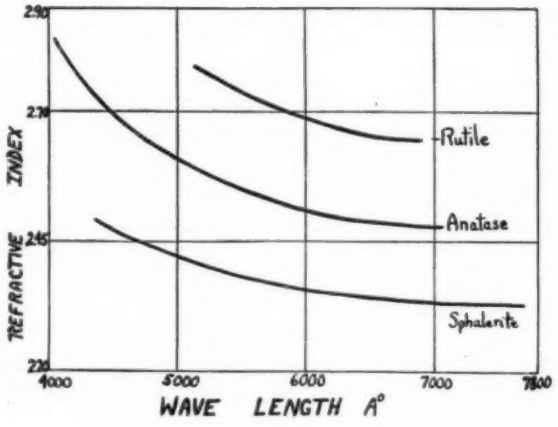

FIG. 10.

CONCLUSION

Pigment materials are selected on the basis of light absorption and refractive index properties. Pigments of high hiding power must have high refractive index. White pigments must be transparent as massive materials, whereas colors must have intense and highly selective absorption. Given a suitable base material, the preparation of a pigment from it is a problem in particle size control. Highest hiding power value is obtained by preparation at a critical particle size of the order of the wave-length of light.

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THE history of research is full of men who duplicated Columbus' experience of hunting for a trade route and finding a continent. It was through effort to create synthetic rubber that the quick-drying lacquers, which have meant so much to the automobile industry, were developed. J. W. Hyatt started experiments to produce synthetic billiard balls, but accidently developed a material for making non-wilt collars and cuffs instead. Then Doctor Baekeland came along with an idea for synthesizing phenol and formaldehyde, but developed a material which makes the ideal synthetic billiard ball, through the discovery of Bakelite *phenolic resinoids. Acheson started out to improve the production of graphite, cooked some coke and sand together, and produced silicon carbide instead. In our own work on fuels, it was an incorrect theory that led us directly to the discovery of the first anti-knock compound, iodine, and later put us on the right track to tetraethyl lead. The point I want to make is that though you end up one hundred and eighty degrees from the thing you may have aimed at, you do end up with something, if you keep working.*

CHARLES F. KETTERING in "Prospecting for Knowledge" in the *Bakelite Review*, January, 1942

The Basic Principles Involved in the Glassy State

BY B. E. WARREN

Massachusetts Institute of Technology, Cambridge, Massachusetts

I. NATURE OF THE GLASSY STATE

GLASS is defined by Morey[1] as an inorganic substance in a condition which is continuous with, and analogous to, the liquid state of that substance, but which, as the result of having been cooled from a fused condition, has attained so high a degree of viscosity as to be for all practical purposes rigid. Glass is well described as an "undercooled liquid," the name suggesting the important idea of reversible continuity with the liquid state, and the fact that glass is a material obtained by cooling down a melt. There is a large but vaguely classified group of materials which are neither liquids nor crystalline solids, which are called "amorphous solids." X-ray diffraction study shows glass to be amorphous, and hence glass can be classed as one branch of the group of amorphous solids. It should be hardly necessary to point out that merely because glass is one kind of amorphous solid, it does not follow that any amorphous solid is a glass.

Some confusion might arise from failure to distinguish between the terms "glass" and "glassy state." There is a well-established popular usage of the word glass to mean a material, an inorganic substance used for bottles and windows. There is a scientific usage of the term "glassy state" to indicate a state of matter. For example, the statement is made that some of the alcohols, when cooled down, often give glassy solids. In scientific usage, the term glass-like state, or glassy state, is used to denote a state of matter in which both inorganic and organic substances may exist. To describe a substance as being in the glassy state, it must be an undercooled liquid, it must have taken on its properties of a solid merely by being cooled down from a fused condition, the increased rigidity by cooling must have been secured without crystallization of the material, the substance should be capable of being carried back and forth from the fused or molten state to the glassy state merely by lowering or raising the temperature without appreciable change in the material when brought back to the same state, and when in the glassy state, the substance should be a brittle amorphous solid exhibiting conchoidal fracture. Amorphous solids which are not produced by the undercooling of a melt cannot be described as being in the glassy state. To classify all such substances as being in the glassy state would make the term synonymous with amorphous solid, which would be contrary to all established usage and to the dictionaries of the English language. Following the established usage of the word glass to mean a material, the discussion in this paper will be limited to the inorganic materials called glass.

Glass-forming materials are ones in which there is sufficient bonding in the melt to produce a highly viscous liquid. The high viscosity produced by transient bonding prevents the atomic rearrangement, necessary for crystallization, when the liquid is brought down to temperatures at which the free energy of the crystalline phase would be lower than that of the randomly bonded structure. The primary conditions for glass-forming ability can be traced through in the following order:

(1) There must be random bonding in the melt to produce a highly viscous liquid.

(2) To allow appreciable bonding in the melt, the free energy $U-TS$ of the randomly bonded liquid must be less than that of either the unbonded liquid or a crystalline solid at the same temperature. This is possible if the energy U of the random structure is not appreciably greater than that of the crystalline solid.

(3) To satisfy condition (2) the scheme of bonding must be so flexible that it is possible to build up a random structure whose energy is not much greater than that of the possible crystalline phases.

A strong but highly flexible scheme of bonding is the necessary condition for glass-forming ability, and this condition is found satisfied in

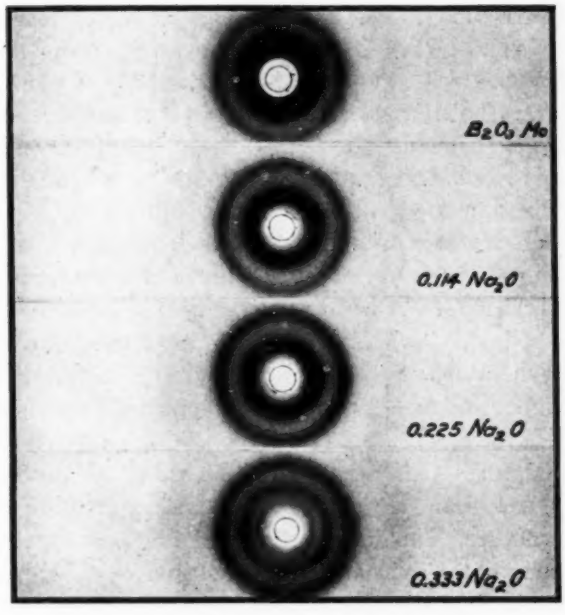

FIG. 1. X-ray diffraction patterns of samples of soda-boric oxide glass. Patterns taken with crystal monochromated Mo$K\alpha$ radiation.

all the true glasses. In vitreous silica each silicon is bonded tetrahedrally to four oxygens, and each oxygen is bonded to two silicons. This scheme of bonding is so flexible that it is possible to build up a random non-repeating network whose energy is not much higher than that of the crystalline forms of silica.

II. SOURCES OF INFORMATION

The present picture of the atomic arrangement in glass has developed from various kinds of information: the laws of crystal chemistry, the x-ray diffraction study of glass, the various measured physical properties of glass, and the kinds of materials and ranges of composition in which glass-forming properties exist.

The x-ray studies of crystalline silicates[2] have established the laws of structural silicate chemistry. These laws have been of great help in building up the present picture of the structure of glass. In all silicates the silicon atom is found to be bonded tetrahedrally to four oxygens at a distance Si$-$O$=$1.62A. Part of the oxygens are shared between two tetrahedral groups, the fraction of shared to unshared oxygens depending upon the silicon-oxygen ratio. It was upon the basis of the established laws of crystal chemistry that Zachariasen[3] predicted the random network structure of glass.

The x-ray diffraction patterns of glass are typical amorphous patterns showing several broad diffuse rings. Figure 1 shows the patterns of a series of soda-boric oxide compositions.[4] Figure 2, showing the patterns of vitreous silica and the devitrified material cristobalite,[5] illustrates the difference between the diffuse ring pattern of the glass and the sharp ring pattern of the crystalline material of identical composition. Figure 3 compares the microphotometer records of three forms of silica: vitreous silica, cristobalite, and silica gel. The silica gel pattern differs from that of vitreous silica by a very strong small angle scattering. The difference is due to the fact that the glass is a homogeneous material, whereas the gel is composed of particles or clusters with gaps or voids between them.[5] From a Fourier analysis of the diffraction pattern, a radial distribution curve is obtained which gives the distribution of neighboring atoms about each atom.[5] The interpretation of the radial distribution curve usually depends upon the previously established laws of crystal chemistry.

Various physical properties, such as density, viscosity, and thermal expansion coefficient, are often very sensitive indicators of structural features or structural changes in the glass. The use of color indicators is a sensitive method of studying changes in valence or changes in coordination number.

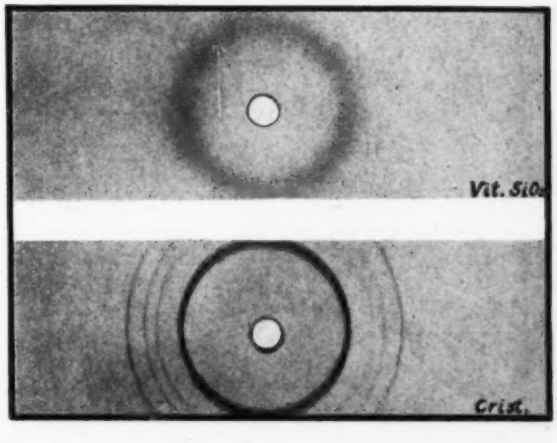

FIG. 2. X-ray diffraction patterns of vitreous silica and cristobalite. Patterns taken with crystal monochromated Cu$K\alpha$ radiation.

III. THE STRUCTURE OF SILICATE GLASSES

Vitreous silica (fused quartz) of composition SiO_2 is probably the simplest glass. The radial distribution function,[6] obtained directly from the diffraction pattern, is shown in Fig. 4. The curve represents two distribution curves superimposed; the distribution of neighboring atoms about a silicon, and about an oxygen atom. The first peak occurs at 1.62A. Since this is the well-known Si−O separation in silicates, it is interpreted as representing the oxygen neighbors about a silicon, and the silicon neighbors about an oxygen. From the area of the peak the number of oxygens about a silicon is calculated as 4.3. Within the experimental error this is taken to be 4, in agreement with the established tetrahedral bonding in silicates. With a composition SiO_2, if each silicon is bonded to 4 oxygens, each oxygen must be bonded to 2 silicons. The next two peaks represent oxygen-oxygen and silicon-silicon neighbors. The Si−Si distance is nearly twice the Si−O value, indicating that the Si−O−Si bond angle is nearly 180°. Definite interatomic distances exist out to the silicon-second silicon distance of about 5.2A. Beyond this value, the distances are random and the distribution curve smooths out.

In vitreous SiO_2 each silicon is bonded tetrahedrally to 4 oxygens at a distance Si−O=1.62A. Each oxygen is bonded to 2 silicons. The Si−O−Si bond angle is nearly 180°, and the relative orientations of the two SiO_4 groups about the connecting Si−O bonds are indefinite. There is a definite structure in vitreous SiO_2, but it is a structure with regard to immediate neighbors rather than a regularly repeating crystalline structure. The local order which exists in the immediate environment of any atom is the same in vitreous silica as in the crystalline modifications of silica. The essential difference between

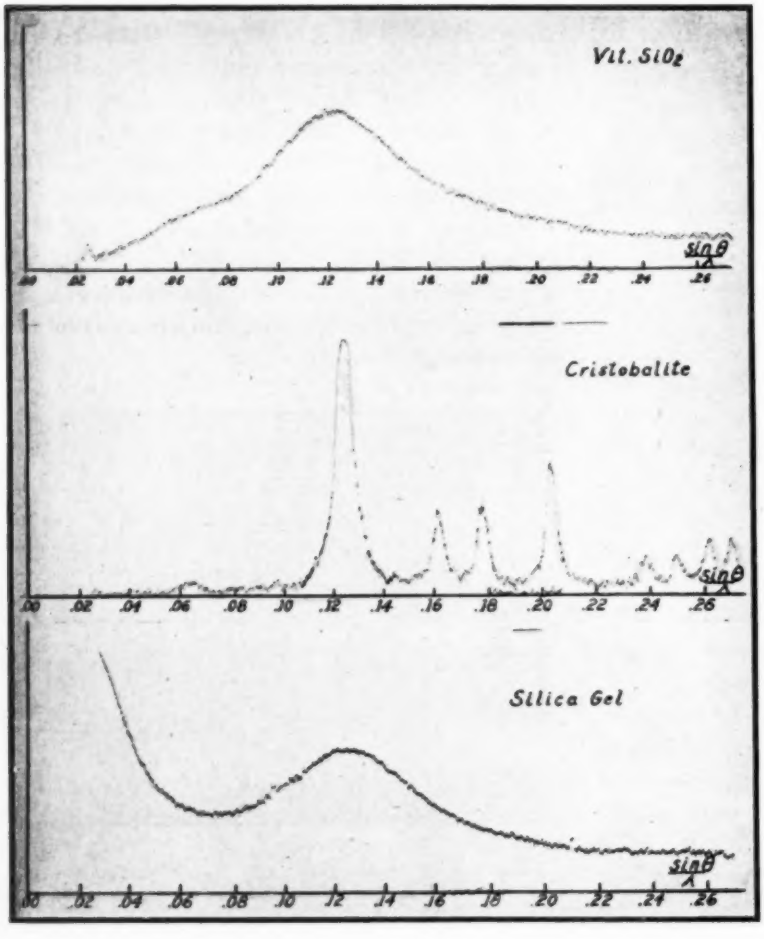

FIG. 3. Microphotometer records of x-ray diffraction patterns of vitreous silica, cristobalite, and dried commercial silica gel.

a glass and a crystal is found in the fact that although essentially the same local order exists in each, the glass lacks the regularly repeating long range order of the crystal. The difference is shown schematically in two dimensions in Fig. 5. Figures 5*a* and 5*b* represent crystalline structures, and Fig. 5*c* the glass.

Figure 6 represents schematically in two dimensions the structure of a soda-silica glass as determined by x-ray study and consideration of the physical properties.[7] Due to the oxygen which was introduced by the soda, the oxygen-silicon ratio is greater than 2, and hence with each silicon bonded tetrahedrally to 4 oxygens, it is impossible for every oxygen to be bonded to 2 silicons. There are two kinds of oxygens; those bonded to two silicons, and those bonded to only one silicon. The sodium ions Na^+ are situated at random in the holes in the silicon-oxygen network, each Na^+ ion having approximately 6 oxygens as immediate neighbors.

Electrolytic conductivity is readily visualized as a stepwise series of displacements of the Na^+ ion through the openings in the silicon-oxygen network. The softening of a silicate glass by the addition of soda is due to the breaks in the silicon-oxygen network which occur wherever there is an oxygen bonded only to one silicon. The greater the soda content, the greater the ratio of singly bonded oxygens to those bonded to 2 silicons, and hence the more breaks in the strong silicon-oxygen network, and the softer the glass. Figure 6 can also be considered as a simplified schematic representation of the structure of the multi-component commercial glasses. The large atom labelled Na might be partly Na, Ca, K, Pb, or Mg. The small network-forming atom labelled Si might be B, P, or partly Al.

IV. EFFECTS OF DISORDER IN VITREOUS SILICA

The thermal expansion coefficient of vitreous silica is extremely small, but the crystalline forms of silica—quartz, tridymite, and cristobalite, have normal values. Expansion can take place by two processes: (1) change in average interatomic distances, (2) configuration changes, such as a change in bond angles. It would be expected that the first effect should be small in silica since the Si—O bond is very strong. The

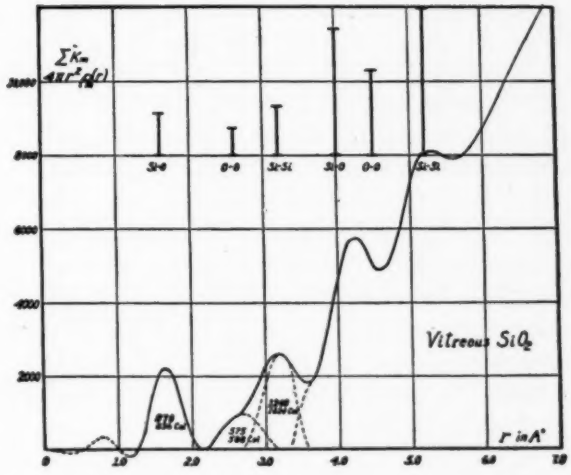

FIG. 4. Radial distribution curve for vitreous SiO_2, obtained by Fourier analysis of the diffraction pattern.

large expansion of quartz is presumably due to the second process.

Figures 5*a* and 5*b* represent schematically certain crystalline modifications of silica. If each of the triangular groups in 5*a* is rotated a few degrees, alternate groups clockwise and counter clockwise, the configuration of 5*b* is produced. Although the interatomic distance is the same, 5*b* represents a smaller volume than 5*a*. If the Si—O—Si bond angle is temperature dependent, a thermal expansion of crystalline silica can result from a change in bond angle. The process can be called a cooperative maneuver, since the possibility of carrying it out depends upon the fact that in the regularly repeating crystalline structure, the clockwise rotation of one group fits exactly with the counter clockwise rotation of the neighboring groups.

Figure 5*c* represents the random network structure of vitreous silica. The lack of a repeating structure precludes the possibility of a co-operative maneuver. Rotations which will increase a particular Si—Si distance will in general cause a decrease in other Si—Si distances. Due to the randomness of the structure, the net change in volume due to rotations of the groups will tend to cancel out. The very small expansion coefficient of vitreous silica relative to quartz could be a direct result of the random structure of the glass. Another effect may also contribute to the abnormally small expansion coefficient of vitreous silica. The x-ray results indicate that the Si—O

−Si bond angle is nearly equal to 180°. At this value any small change in the angle will produce an extremely small change in the Si−Si distance.

Bridgman has found that for small pressures the compressibility of vitreous silica increases with pressure, whereas for quartz it decreases. It has been found by von Hippel and Maurer[8] that the electric breakdown strength of quartz increases with temperature at room temperature, but that for vitreous silica it decreases with increasing temperature. They attribute the difference in dielectric behavior to the difference between the ordered structure of the crystal and the disordered structure of the glass.

V. IMMISCIBILITY IN THE LIME-SILICA SYSTEM

The problem of immiscibility in glass melts is an interesting variation of the disorder problem. A rough free energy treatment of the problem of immiscibility in the lime-silica system will be used as an example.[9] Figure 7 shows the equilibrium diagram for the lime-silica system. For small lime content, and temperatures above 1700°C, the melt consists of two immiscible liquids. We wish to investigate the factors which determine the boundary between the two-phase liquid region and the single phase region.

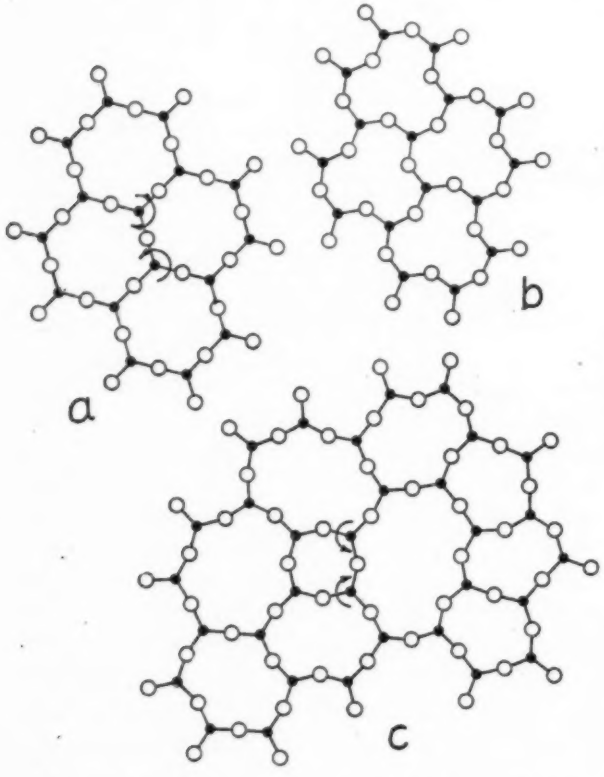

FIG. 5. Schematic two-dimensional figures to illustrate the difference between the regularly repeating structure of a crystal and the random network of a glass. *a* and *b*, crystalline structures; *c*, glass.

Consider a single phase lime-silica melt (liquid B) with the smallest lime content that can produce a single-phase liquid. There will be oxygens bonded to 2 silicons, and oxygens bonded only to one silicon, since the total number of oxygens is greater than twice the number of silicons. The oxygens which are bonded only to 1 silicon are unsaturated, and each Ca^{++} ion tries to surround itself by several of these single-bonded oxygens. Because the number of single-bonded oxygens is twice that of calcium atoms, and in order that each calcium shall have a reasonable number of surrounding oxygens, it is necessary for each single-bonded oxygen to bond to more than 1 calcium. Two calciums bonded to the same oxygen cannot be farther apart than twice the Ca−O distance.

$$\text{Ca}-\text{Ca}=2\text{Ca}-\text{O}=2\times 2.38=4.76\text{A}.$$

For a homogeneous glass with atoms uniformly distributed, the volume of glass containing 1 calcium atom will be of the order of magnitude of the cube of the linear separation.

$$\text{Vol./Ca}=(4.76)^3=108\text{A}^3.$$

Let us represent the composition as X percent by weight of CaO and $(100-X)$ percent by weight of SiO_2. The volume per calcium atom can then be expressed in terms of the composition X, the density, the molecular weight of CaO, and the Avogadro number.

$$\text{Vol./Ca}=\frac{100\times 56.1\times 10^{24}}{\rho\times 6.06\times 10^{23}X}.$$

For the range of composition of interest, ρ has an average value of about 2.6. Equating the two values for the volume per calcium atom, and solving for the composition, we find $X=33$ percent.

This means that for compositions in which the lime content is less than about 33 percent, the Ca^{++} ions and the single-bonded oxygens are

too few in number and too widely separated for each to be surrounded by a proper number of the other. For a lime content of less than about 33 percent, the energy of the single-phase liquid is higher than the energy for a two-phase liquid in which the lime has segregated into one of the phases so as to bring the content of that phase up to 33 percent.

The behavior of the system is of course determined by the free energy, the system segregating into two phases when the free energy of the two-phase system becomes less than the free energy of a single-phase system. Since this is only a qualitative discussion of free energy, consideration will be given only to an energy difference resulting from whether or not the Ca^{++} ions and single-bonded oxygens have proper surroundings, and to a temperature entropy difference for which the entropy difference is essentially the increased entropy of the single phase caused by the entropy of mixing. The three-coordinate diagram in Fig. 8 shows these two differences as a function of temperature and composition.

For a lime content of less than about 33 percent, the energy of the single-phase becomes greater than that of the two-phase system. This is approximately independent of temperature, and the energy difference $U_{SP}-U_{TP}$ is represented by the tunnel-shaped surface running parallel to the temperature axis. As a result of the entropy of mixing, the entropy of the single-phase is greater than that of the two-phase system. The temperature-entropy difference $TS_{SP}-TS_{TP}$, is shown by the surface marked TS; it increases proportionally to T for a given composition, and it increases with the percentage of lime* for a small lime content. The line of demarcation between the single-phase and the two-phase region is the line along which the two free energies are equal.

$$F_{SP}-F_{TP}=(U_{SP}-U_{TP})-(TS_{SP}-TS_{TP})=0.$$

This will be given by the intersection of the two surfaces. The form of the intersection is suggested qualitatively by the dotted curve of Fig. 8. This dotted curve is intended to represent the boundary of the region marked liquids A and B on Fig. 7.

The limit of immiscibility on the high lime side shifts to lower lime content as the temperature increases. Above temperatures corresponding to the peak of the curve, there is complete miscibility for all compositions. The present treatment is not intended to be more than qualitative. The only quantitative calculation involved is the composition 33 percent, below which the energy of the single phase becomes appreciably greater than the energy of a two-phase system. The approximations involved in the calculation of the composition 33 percent are sufficiently rough so that the value has no great accuracy. The treatment is not intended to do more than to suggest the nature of the atomic processes which determine the miscibility and immiscibility in a glass system such as lime-silica.

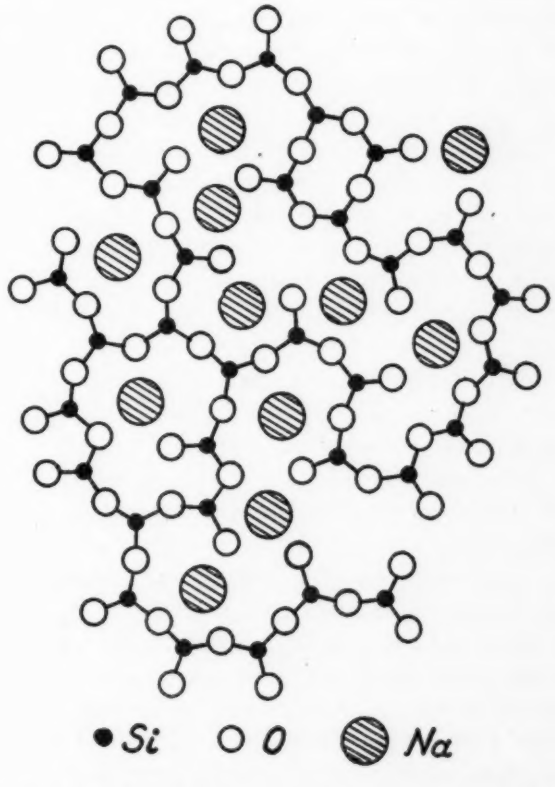

FIG. 6. Schematic representation in two dimensions of the structure of soda-silica glass. To correspond to two dimensions, the silicons are shown bonded only to three oxygens.

* The shape of the TS surface, as a function of composition, is given qualitatively by assuming it to be similar to the curves which have been calculated for the entropy of mixing of two gases.

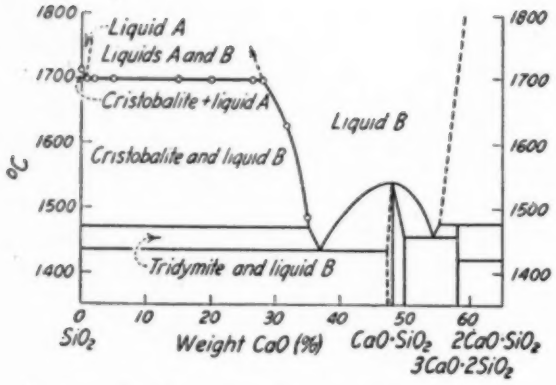

FIG. 7. Equilibrium diagram of the system $SiO_2-2\,CaO\cdot SiO_2$ (J. W. Greig).

VI. THE BORIC OXIDE ANOMALY

Vitreous B_2O_3 is a glass in which each boron is bonded to three oxygens and each oxygen to two borons. Since each BO_3 group is bonded to the surrounding atoms in only three directions, it would be expected that the structure would be much weaker than vitreous silica. Whereas silica glass has a very small coefficient of thermal expansion, the value for vitreous B_2O_3 is quite large. When SiO_2 is added to B_2O_3, the thermal expansion drops rapidly since each tetrahedral SiO_4 group bonds to the surrounding structure in four directions. The more SiO_2 in the structure, the more bonds per cation and the more tightly the structure becomes knit together. If m is the weighted average coordination number of the glassforming cations, it will vary from 3.0 for B_2O_3 to 4.0 for SiO_2 for the system $B_2O_3-SiO_2$. In Fig. 9 the expansion coefficient for the system $B_2O_3-SiO_2$ is plotted against the average coordination number m.

When a small amount of soda is added to B_2O_3, the extra oxygen introduced by the soda allows part of the borons to change over from triangular to tetrahedral coordination. If each oxygen is assumed to be bonded to 2 borons, the number of borons in tetrahedral coordination can be readily calculated for each soda content. The borons in triangular and tetrahedral coordination have 3 and 4 bonds, respectively, so that the average coordination number m can be computed for each composition. The expansion coefficient for the system $Na_2O-B_2O_3$ is plotted in Fig. 9 against the average boron coordination number m, assuming that as many borons as possible have changed to tetrahedral coordination at each composition.

The comparison of the two curves is rather striking. Starting from the composition B_2O_3, the addition of soda produces exactly the same drop in expansion coefficient as the addition of silica, when the compositions are expressed in terms of average coordination numbers. The Na−O bonds are too weak to be of much importance, and the expansion coefficient depends only on the average number of strong cation bonds. The increase in the cation coordination number from 3 to 4 is equivalent, whether it is made by changing a boron atom from triangular to tetrahedral coordination, or by replacing a triangularly bonded boron by a tetrahedrally bonded silicon.

The two curves separate sharply at an average coordination number of $m=3.17$, corresponding to a $Na_2O-B_2O_3$ composition of 13.0 percent of Na_2O. This evidently is the composition at which the extra oxygen introduced by the soda ceases to be used up by boron atoms changing to tetrahedral coordination. From this point on, there is an increasing number of oxygens bonded only to 1 boron. The expansion coefficient increases with increasing soda content, similar to the behavior in a soda-silica glass.

Two questions that immediately suggest themselves are (1) why do as many as possible of the borons change to tetrahedral coordination for small soda content, and (2) why does this process stop at a composition of about 13 percent of Na_2O? The answer is given by the same kind of considerations that have been used in discussing the problem of immiscibility. If a small amount of soda is added to B_2O_3 and all of the borons remain in threefold coordination, there will be two kinds of oxygens, namely, those bonded to 2 borons and those bonded only to 1 boron. The sodium ions, Na^+, will try to surround themselves by the unsaturated single-bonded oxygens. The number of Na^+ ions and of unsaturated oxygens is too small at small soda content, and they are consequently too widely separated for this to be accomplished effectively. On the other hand, if as many as possible of the borons change to tetrahedral coordination, there will be four times as many unsaturated oxygens and there-

fore a much better possibility for the Na^+ ions to surround themselves by unsaturated oxygens. The change takes place merely to produce a structure of lower energy. When the soda content gets high enough for the Na^+ ions and unsaturated oxygens to be present in sufficient numbers to provide suitable surroundings for each other, the need for further change decreases rapidly.

This limiting composition can be calculated with a few simple approximations. Assume that each oxygen is bonded to 2 borons and that as many as possible of the borons are in tetrahedral coordination. Each oxygen in a boron-oxygen tetrahedral group is unsaturated, inasmuch as a trivalent cation B^{+3} has half-interest in 4 divalent negative oxygens. Each tetrahedral group must contact 2 sodium ions to satisfy the unsaturated oxygens (because 1 sodium cannot touch all 4 oxygens). From the known interatomic distances $B-O=1.50A$ and $Na-O=2.35A$, this gives an approximate $Na-Na$ distance of 5.7A.[9] The volume per sodium will be of the order of magnitude of this distance cubed.

$$\text{Vol./Na}=(5.7)^3=188\text{A}^3.$$

Following the same procedure as used in the discussion of immiscibility, this volume can be expressed in terms of the composition. Solving we find $X=12$ percent Na_2O. This value should represent the composition at which there is no further need for complete change to tetrahedral coordination. The value is to be compared with the composition of 13 percent at which the two curves of Fig. 9 separate.

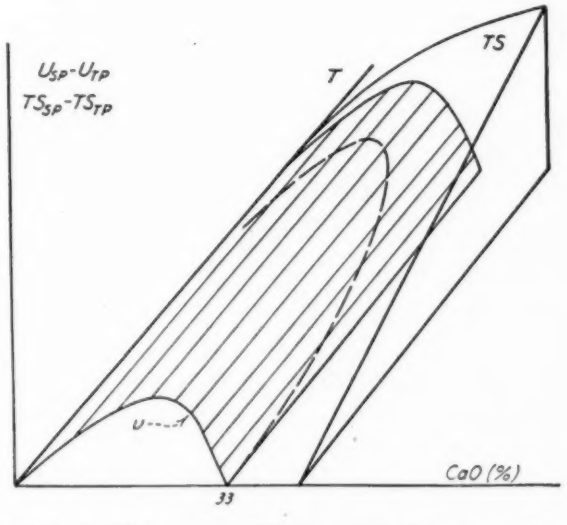

FIG. 8. The energy difference and the temperature-entropy difference which determine the limit of immiscibility in the lime-silica system.

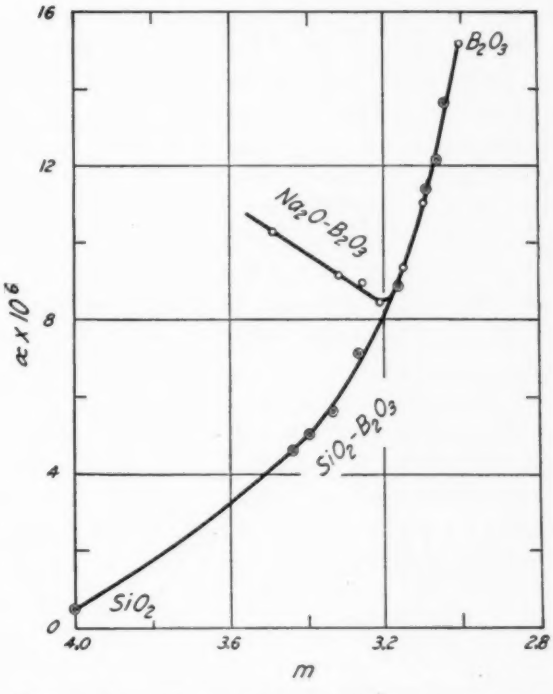

FIG. 9. Thermal expansion coefficients *vs.* average coordination number m for the systems $SiO_2-B_2O_3$ and $Na_2O-B_2O_3$.

The approximations involved in the foregoing calculation are rather rough, and the excellent numerical agreement is therefore largely fortuitous. The important point is that from these calculations some insight is gained of the significance of the anomalies in the soda-boric oxide system. All extra oxygen introduced by the soda, at low soda content is used up in changing boron atoms into tetrahedral coordination to provide better surroundings for the Na^+ ions. There are enough unsaturated oxygens above the calculated composition to provide proper surroundings for the Na^+ ions, and further changing of boron atoms into tetrahedral coordination becomes rapidly unnecessary.

VII. DISCUSSION

The materials which are used in commercial glasses can be roughly classified into two groups: network formers and modifiers. Na_2O, K_2O, CaO, MgO, and PbO are typical modifiers; they

cannot by themselves form a glass, but can modify the properties of a glass into which they are introduced. SiO_2, B_2O_3, and P_2O_5 are the typical network-forming oxides. Si and P are probably always in tetrahedral coordination, while B may be in either triangular or tetrahedral coordination. In addition there are a few oxides which may be in an intermediate group. From the study of crystalline alumino-silicates, it is well established that the Al atom is sometimes in sixfold coordination and sometimes in tetrahedral coordination replacing the silicon. It is likely that Al^{+++} and probably Fe^{+++} are to some extent in tetrahedral coordination replacing Si in the complex glasses. In discussing silicate glasses, the loose statement is made that the structure and glass-forming properties depend primarily upon the oxygen-silicon ratio. Actually it is of course the ratio of oxygen to the total number of network cations including silicon and all the other cations in three- or fourfold coordination which are effectively substituting for silicon.

The glassy state offers an interesting field for study. In a glass many properties such as composition can be changed continuously. Studies can be made on a material which can be changed continuously from a true liquid to a form having most of the properties of a solid. For many purposes a glass at room temperature represents the frozen-in disorder which is characteristic of a much higher temperature.

The picture of glass which has been presented in this paper is certainly only a first-order approximation. Many well-established facts, such as the conditioning of a glass at various temperatures, will probably require the refinements of the next order approximation, for a complete understanding. Although x-ray diffraction study has contributed much to the first-order picture, it is doubtful if it can do much more. Studies of glass are being made by a wide variety of techniques. The study of physical properties such as density, viscosity, thermal expansion, and elastic constants, the studies by Raman and infra-red spectra, the measurements of dielectric constants, and the effects on color indicators are all contributing toward a final picture. Eventually all this information must be and will be fitted into one unified picture of the glassy state.

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The Physics of Pigments in Dispersed Systems

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IT takes only a slight acquaintance with the literature before one becomes conscious of the fact that there exist two types of minds that approach the science of rheology along quite different paths. The first of these is the academic, the second, the industrial.

The academic investigator is interested to a large extent in the Einstein and Staudinger equations; he deals with suspensions of colloidal particles in vehicles, but always at such extreme dilutions that interaction between the particles is thought improbable. He is not interested in states of aggregation, though he does give considerable thought to the effect of particle shape. His language and technique are practically unknown in many industries where rheology is employed.

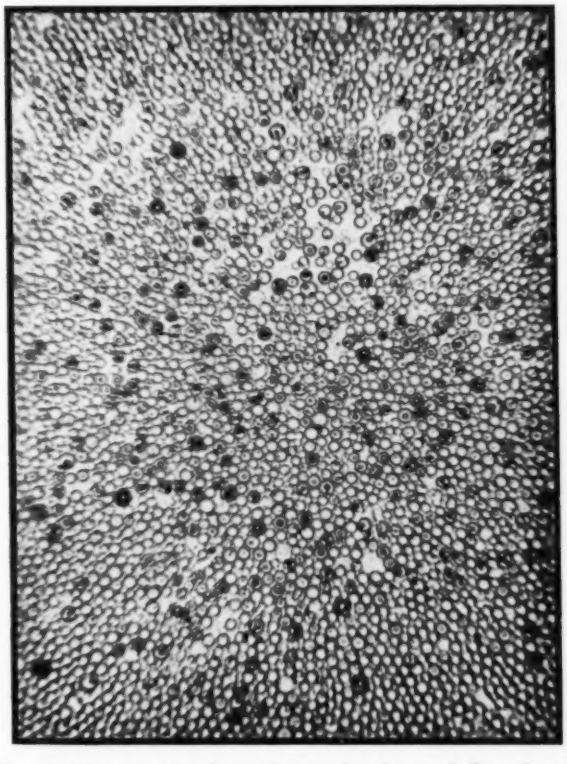


FIG. 1. Microscopic glass spheres showing a deflocculated structure. (250×)

On the other hand, the industrial rheologist must be a realist. He is compelled to deal with things as substantial and prosaic as paints, enamels, and printing inks. Such products are likewise suspensions of particles in vehicles, but at concentrations so high that particle interaction is inevitable. The industrial rheologist, then, is not only interested in particle size and shape, but, in addition, he is deeply concerned with states of aggregation or structure. It is his lot to study the physics of systems composed of non-uniform particles ranging from the submicroscopic upward, in every state of aggregation, and all suspended in mixed vehicles composed of anything from Newtonians to highly polymerized pseudoplastics.

As though this were not enough nature has conspired further. For reasons not yet clearly understood, such systems are invariably thixotropic. This adds to the complexity by causing the materials to "break down" as soon as the investigator attempts to secure measurements upon them by devices such as viscometers.

It is evident that the industrial rheologist should not attempt to visualize structure unless recourse be had to the microscope. Unfortunately, it takes time to develop adequate microscopical technique for such work, so few rheologists employ it. Consequently, very little will be found in the literature showing the relationship between the pigment structure, as revealed by the microscope, and the rheological properties of the suspension itself.

I. THE MICROSCOPY OF PIGMENTS

A material is considered to be a pigment only when it is insoluble in the vehicle in which it is used. A pigment need not necessarily have hue. There are many white pigments, such as titanium dioxide, lithopone, zinc oxide, the various white leads, etc. There are also black pigments. These are composed mainly of carbon. Gas black is made by burning natural gas. Lamp black is the

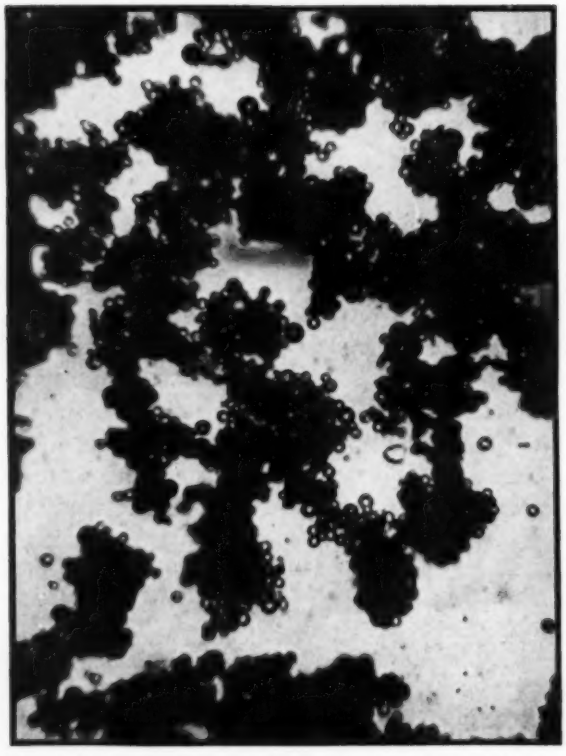


FIG. 2. Microscopic glass spheres immersed in methylene iodide, showing flocculated structure. (250×)

soot obtained from burning oil. There are also other blacks such as bone blacks and acetylene blacks.

If a colored pigment is soluble in its vehicle, it might be classified as a dye, but never as a pigment. One of the principal functions of a pigment is to hide the surface over which it is spread. The ability to do this is referred to as "covering power." Good covering power depends on suitable particle size and refractive index. The works of Stutz and Pfund[1] have indicated that the correct particle size for maximum coverage is approximately one-half the wave-length of the light used in viewing the material.

When the particle size is either larger or smaller than this critical value, covering power falls off. It can readily be understood, then, that if the pigment goes into solution, its particle size is reduced to molecular dimensions and its covering power is thereby lost. Pigments of low refractive index also have low covering power. This arises from the fact that the refractive indices of the pigment and vehicle are brought closer together and the system becomes more nearly optically homogeneous. Such pigments are desirable for manufacturing the so-called transparent inks.

The total number of different pigments that have been produced commercially runs into the thousands. All of these, however, are not in general use. A practical list of the most commonly used pigments would include such as the following:

White: Titanium dioxide, basic carbonate of white lead, basic sulfate of white lead, lithopone, zinc oxide, and zinc sulfide.
Black: Gas black and lamp black.
Yellow: Chrome yellows and Hansa yellow.
Orange: Chrome orange.
Blue: Alkali blues, iron blues, peacock blue, ultramarine, and the phthalocyanines.
Reds: Lithols, toluidines, eosines, and iron oxides.
Greens: Chrome greens, chromium oxide.

The average particle size range covered by these pigments extends from about 0.01μ to 1.0μ and over. The *ultimate particle* is a single crystal

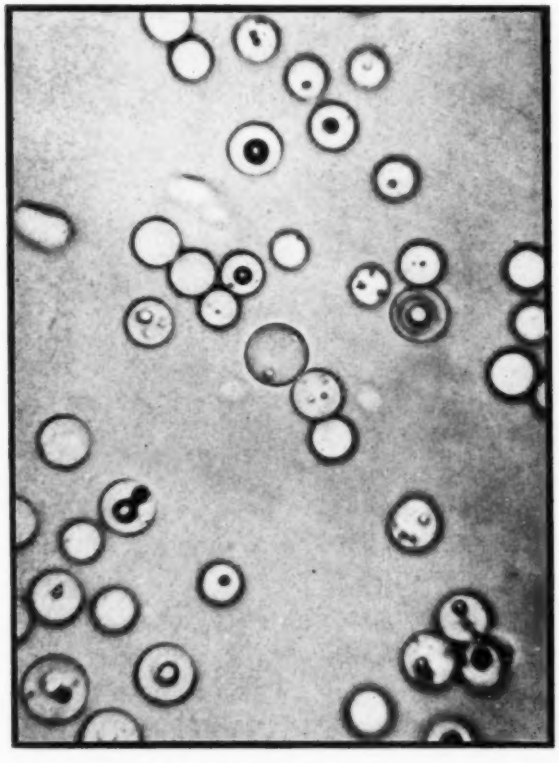


FIG. 3. Particles pushed together to form a group. This group is permanently dispersed on moving the coverglass. (1050×)

or fragment of a crystal. The carbon blacks constitute perhaps the only exception to this generalization.

Groups of ultimate particles firmly stuck together form what will be called here a *hard aggregate*. These groups function rheologically as single particles by maintaining their size and shape during the time of their commercial application. Such hard aggregates will, therefore, be called *ultimate working units*, though it should be understood that single particles also come under this classification.

The ultimate working units in calcined products like lithopone and titanium dioxide are likely to be small firm aggregates. This is seen when examining such materials with an electron microscope. In cases of fumed products, like zinc oxide, the ultimate working unit is invariably a single crystal particle, fragment, or an aggregate formed by twinning. With precipitated pigments that are not calcined but filtered and dried, the ultimate working unit is usually a mixture of both hard aggregates and ultimate particles.

There is no way of measuring particle size that is entirely free from objection. The microscopical method[2] has many weak points; nevertheless, it is sufficiently direct and fundamental to be employed as a basis for calibrating other methods of a more indirect nature. When pigment particles possess a high degree of uniformity and the size falls within a range extending from about 0.2μ to 2.0μ, then conditions are suitable for ordinary white light microscopical measurements. The electron microscope, on account of its much greater resolving power, can measure particles perhaps as small as 0.01μ or even less.

The customary procedure in making a particle size measurement is to produce a size-frequency curve. This is accomplished, first by photographing a sample of the pigment at a carefully ascertained magnification, and then, by means of a lantern, projecting this picture onto a screen, also at a precisely known magnification. The product of these two magnifications is the total magnification, which is divided into the average measurement of several hundred or more particles measured on the screen, when obtaining the actual average particle size.

A total magnification of 20,000 diameters is convenient for measuring a normal size pigment.

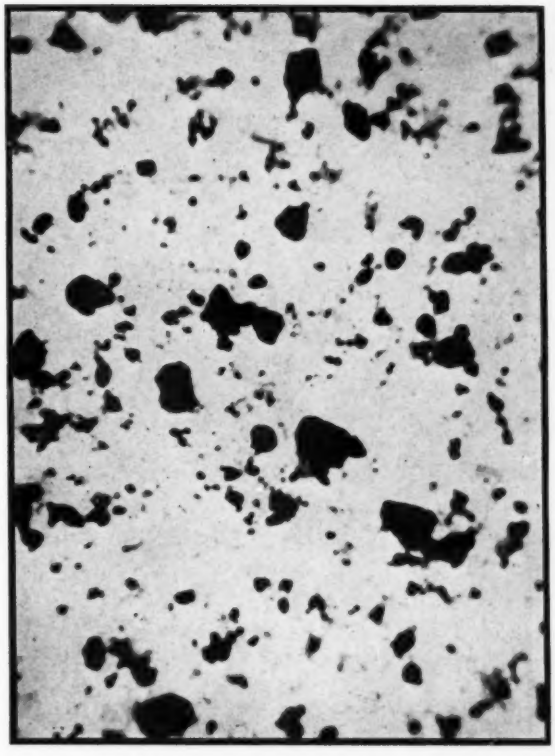
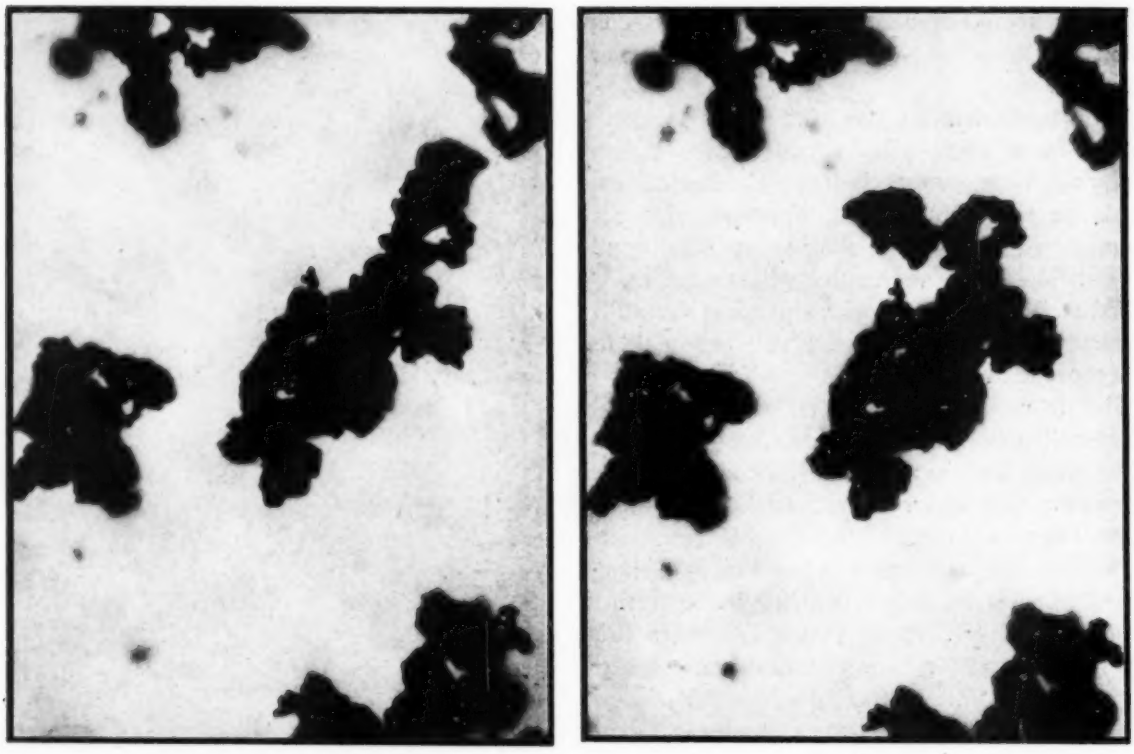


FIG. 4. Particles cemented together forming a hard aggregate. These aggregates function as individual particles and do not disperse on moving the coverglass. (250×)

The horizontal diameter of the particle constitutes a sufficient measurement where the particles are not too acicular or not too plate-like. Since the particles are oriented in every possible direction this procedure will give a fair average. It should be pointed out that when the particle is less than half a micron in diameter its image, even under the best white light microscopical conditions, is not a true geometrical representation of the particle outline. If the particle is a parallelogram in cross section, the corners will not appear sharp angled but will be curved. This arises from diffraction and the insufficiency of resolving power of the lens system. As the particle becomes smaller the curved corners occupy a greater portion of this image until finally the image is all curved corners and appears circular. Single transparent particles above 0.3μ will be clear centered; below this size they will be all edge and look like solid black dots. Below 0.2μ these black dots lighten and become more greyish; and below 0.1μ they vanish from view



Before disturbing. (400×)

After disturbing. (400×)

FIG. 5. Carbon black flocculates before and after disturbing under coverglass. Shows particles held together by the force of flocculation. Particles cannot be cemented together for they were originally dispersed.

entirely. From this region downward the electron microscope has supreme command.

The fact that the geometrical image of small particles is modified by diffraction is not necessarily such a serious matter as might be judged at first, for the errors in measurement of many particles oriented in various ways are just as likely to be negative as positive. Consequently, a measurement consisting of the average of several hundred particles or more will give surprisingly dependable results.

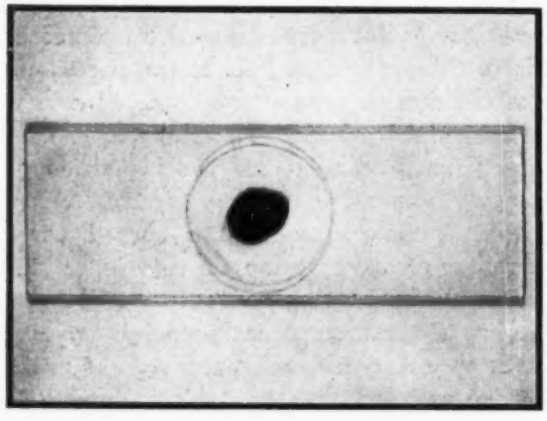


FIG. 6. Drop of ink covered first with a drop of its own vehicle and then squeezed out slightly under coverglass.

There are various average diameters that must be considered. These are not convertible one into another. They can all be derived, however, from the distribution curve. The most useful average diameter is the one related to the specific surface of the material by the following:

$$S=\frac{\sigma'/\nu'}{\rho d_3}, \tag{1}$$

where S is the surface in meters per gram; σ' and ν' are shape factors;[3] ρ is the density; and $d_3=\sum nd^3/\sum nd^2$ is the average diameter. There are other average diameters of importance. The arithmetical mean diameter, $d_1=\sum nd/\sum n$; and $D=(\sum nd^3/\sum n)^{\frac{1}{3}}$, the diameter related to the number of particles N per gram by the equation

$$N=\frac{1}{\rho\nu' D^3}. \tag{2}$$

II. THE MICROSCOPY OF PIGMENT SUSPENSIONS

Particle interaction takes place when the pigment-vehicle ratio is sufficiently high to bring about particle contact. It is never possible, however, to observe two particles exerting a force of attraction on each other over a distance large enough to be resolved by the microscope. The attracting force, giving rise to pigment flocculation, does not extend very far beyond the pigment surface. If van der Waals forces are responsible for the attraction, the distance over which they operate effectively cannot be much greater than the order of the dimensions of the vehicle molecule.

Pigment flocculation occurs in the following manner: The dry pigment powder is rubbed or ground into the vehicle. During this operation the soft pigment lumps are dispersed into their individual particles or into any other form that the ultimate working unit might take. The vehicle presumably comes into contact with the entire pigment surface. The process of rubbing or grinding sets up convection currents in the vehicle that subside only after grinding has ceased; therefore, any particles momentarily dispersed by the grinding action can be forced together again by operation of the convection currents. In other words, flocculation can occur even though the force of flocculation does not extend to any great distance beyond the particle surface.

No attempt will be made here to explain the nature of the force of flocculation. It is necessary only to recognize the existence of this force. It has been known for some time that powders flocculate in vehicles that wet them poorly. Two striking examples might be mentioned: sulfur in water and glass in methylene iodide. In both cases the contact angles are high, indicating poor wetting. Sulfur is well known for its inability to be wet by water, and every microscopist knows that methylene iodide will not stick to glass slides and rods.

Both powdered sulfur in water and powdered glass in methylene iodide give a high force of

FIG. 7. Flocculated boundary line under microscope. (125×)

FIG. 8. Deflocculated boundary line under microscope. (400×)

flocculation. Though these forces, naturally, cannot be seen, they do manifest themselves in a way that is easily demonstrated under the microscope. A group of particles might exist either because the particles were pushed into contact, in which position they remain on the microscope slide until disturbed, or the group might be the result of a force of flocculation holding it together (compare Figs. 1 and 2); also a group can exist because the particles of which it is composed are cemented together forming a hard aggregate. Which particular group exists can be determined by proper manipulation of the cover glass.

If moving the cover glass permanently disperses the particles, then the group was formed simply by forcing the particles together (Fig. 3). If the group rolls around without changing its size or shape, it is a hard aggregate (Fig. 4). If the group disperses and then reforms when the convection currents cease, it is a flocculate (Fig. 5). That there is a force holding a flocculate together can be ascertained by pressing down the cover glass with a needle point in the neighborhood of the flocculate. The flocculate can be compressed and disturbed without the individual particles becoming detached, showing that they are being held together by a very definite force. It will be shown later how this force manifests itself in the rheological consistency curve.

When the situation is such that the pigment particles flocculate, the flocculates themselves—

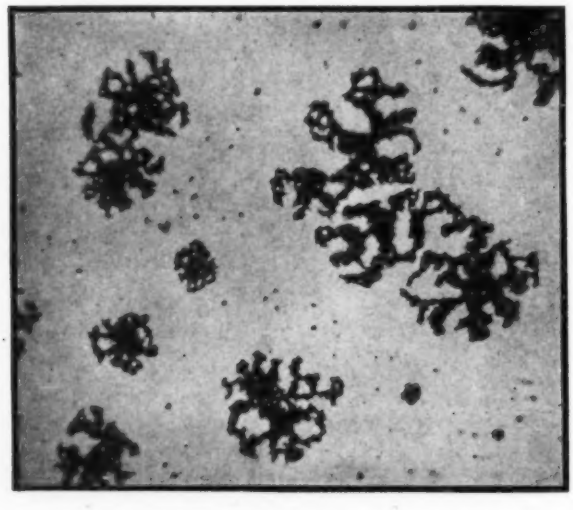


FIG. 9. Branched flocculates indicating particle orientation. (500×)

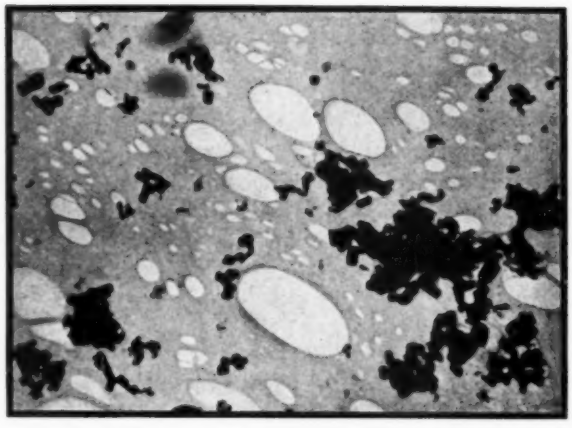


FIG. 10. Electron micrograph of fine grained zinc oxide. Shows types of flocculation illustrating method of particle readjustment as described in text. (12,750×)

which are simply pigment clusters—will also flocculate. The net result is a flocculated structure, the individual flocculate losing its identity in much the same manner that a sodium chloride molecule loses its identity in a sodium chloride crystal. It becomes meaningless, therefore, to talk about the size of a flocculate as one would in mentioning the size of a hard aggregate or of an ultimate particle.

Flocculation creates a pigment structure held together by what has been called here the *force of flocculation*. Before this structure can be sheared, i.e., made to flow plastically, this force must be matched by an equal and opposite force externally applied. Only after this very definite force has been exceeded can flow take place. This is the origin of yield value,[4] the rheological factor that distinguishes plastics from Newtonians.

If a drop of printing ink is compressed between a cover glass and a microscope slide into a very thin film and examined microscopically, it will be observed that the particles are so closely packed together that nothing much can be learned about structure. The following technique has been developed to surmount this difficulty. It is always possible to dilute a suspension with some of its own vehicle without changing the nature of its structure. The vehicle can always be obtained by centrifuging, if it cannot be had otherwise. A very small amount of the suspension is placed on the middle of a microscope slide. A large drop of its vehicle is then placed on top of it and allowed

to flow over and around it. This is then covered and the cover glass pressed down carefully with a slight rotary motion (Fig. 6). This motion will cause the pigment structure to open up at the boundary between suspension and vehicle by dispersing it slightly into the surrounding vehicle. The boundary line is now examined with the microscope.

It will be seen, if the structure is a flocculated one, that the pigment does not disperse readily into the surrounding vehicle (Fig. 7). However, it will spread out sufficiently for the microscopist to observe the nature of the structure. No Brownian motion is likely to be detected either in the flocculated mass or in any of the loose particles that might have become detached. This relative absence of Brownian motion is a corroborative check on the presence of flocculation. If the particle is too large or the vehicle too viscous, Brownian motion might not be apparent even when flocculation is absent.

If the structure is a deflocculated one, the pigment readily flows out into the surrounding vehicle (Fig. 8), often producing streamline patterns by following convection currents. Brownian motion will be detectable particularly under high magnification. The presence or absence of Brownian motion is a point of some importance. Even though the particles are small enough to give a detectable amount of Brownian motion, there are times when this motion seems to be absent. This state of affairs exists, at least partially, when there is poor wetting between particle and vehicle. Since this is also the condition for producing flocculation, the relation between Brownian motion and flocculation becomes evident.

The phenomenon of thixotropy has always been associated with structure. It should not be assumed that in the case of thixotropic paints and printing inks this structure necessarily is the one arising from pigment flocculation. It is probably true that pigment flocculation is a prerequisite for thixotropy but it is not yet proven that the pigment structure is the actual thixotropic structure. Since the time interval for thixotropic build-up is a relatively large one, it is reasonable to suppose that either some form of particle orientation or of particle readjustment is involved in the process. The particle in question might be the pigment particle or it might be the polymerized molecules of the vehicle.

Occasionally some evidence arises indicating that pigment particles possess a certain amount of orientation when flocculated. This is true of the highly branched flocculates (Fig. 9). On the other hand microscopic glass beads, so spherical that orientation seems impossible, have been made into thixotropic suspensions. In this case one is almost forced to visualize the thixotropic

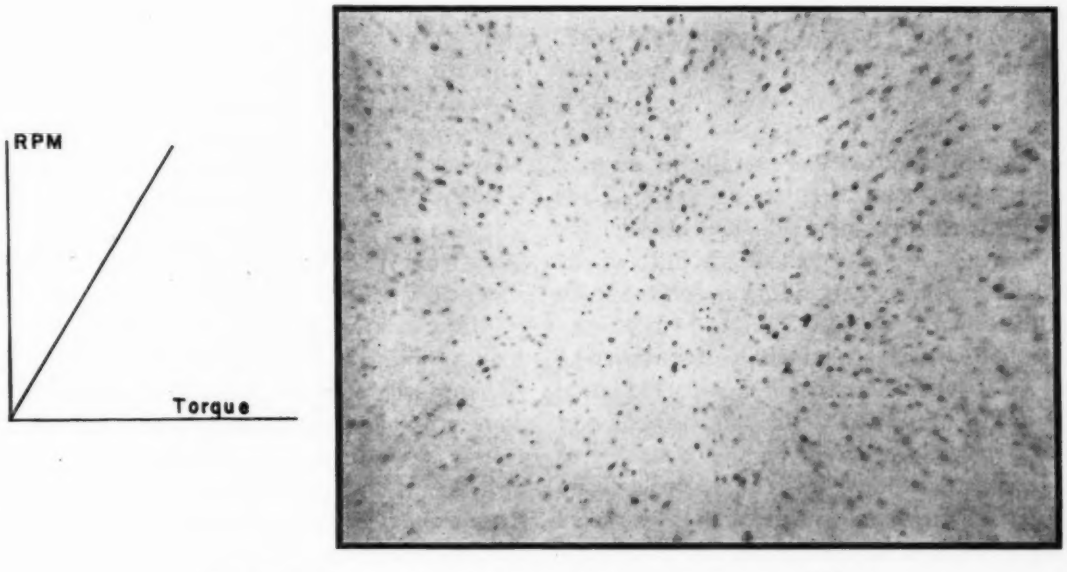


FIG. 11. A Newtonian suspension and its consistency curve. (500×)

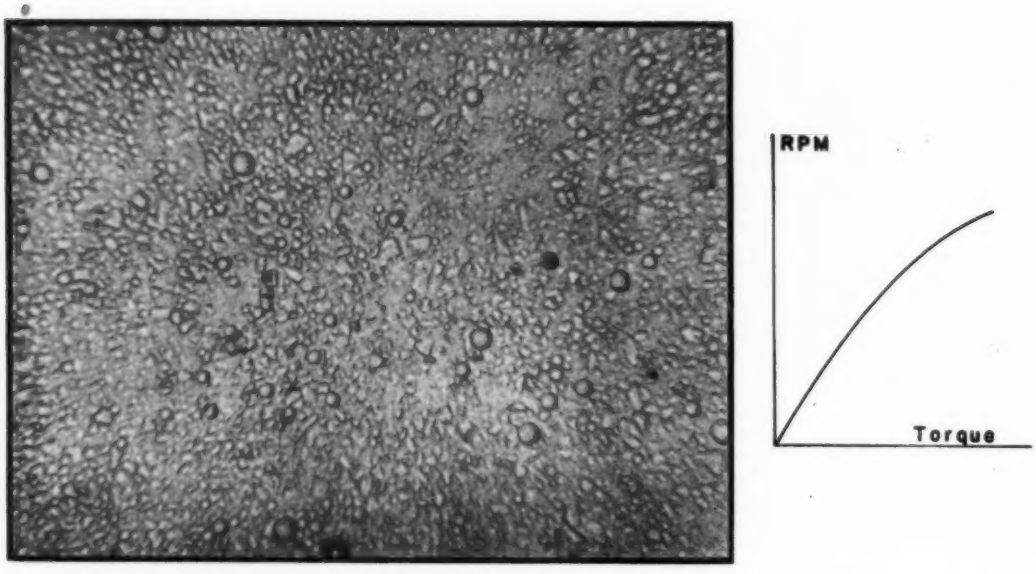


FIG. 12. A dilatant suspension and its consistency curve. (800×)

structure as existing in the molecules of the vehicle between the particles.

Except for spherical particles, a thixotropic model can be visualized where gradual particle readjustment takes the place of gradual orientation. For instance, if the particles are crystalline, flocculation might build up in steps by progressive flocculation at corners, edges, and faces. In regard to edges and faces, contact could vary over any fraction thereof up to the entire edge and face. Such progressive readjustment could be brought about by forces of attraction which would be operative over the minute distances existing between flocculated particles. (See Fig. 10.)

In regard to orientation, time would increase the number of oriented bonds. In the case of particle readjustment, time would increase the strength of the individual bond. In either case the net result would be an increased strength of the thixotropic structure demanding a greater force to break it down.

Occasionally it is stated that, since stirring mechanically deflocculates a pigment, yield value should disappear under the circumstances and should not manifest itself in the consistency curve. It is evident that this conception can be erroneous because yield value does not result from structure *per se* but from the force of flocculation which creates the structure. In a crowded system such as exists in commercial products like paints and printing inks, stirring cannot substantially increase the average distances between the pigment particles and, therefore, cannot materially affect the force of flocculation.

If stirring permanently destroyed structure so that it would not reform when stirring ceased, then yield value could not be measured. This does not happen, however, in flocculated or in orientated systems. The endeavor to reflocculate and to re-orientate is continuously present. Therefore, in order to maintain a state of mechanical deflocculation or of deorientation, the continuous application of an external force is necessary. This force manifests itself in the consistency curve and is directly related to the yield value of the system.

III. THE RHEOLOGY OF PIGMENT SUSPENSIONS

Many devices have been invented for measuring consistency of industrial products of the pigment-vehicle type. Though these instruments sometimes possess certain technical value for control work, they are often faultily constructed or incorrectly employed, and thereby give data of little value for rheological purposes.

The thing that is essential for securing useful rheological data is to be able to measure the rate

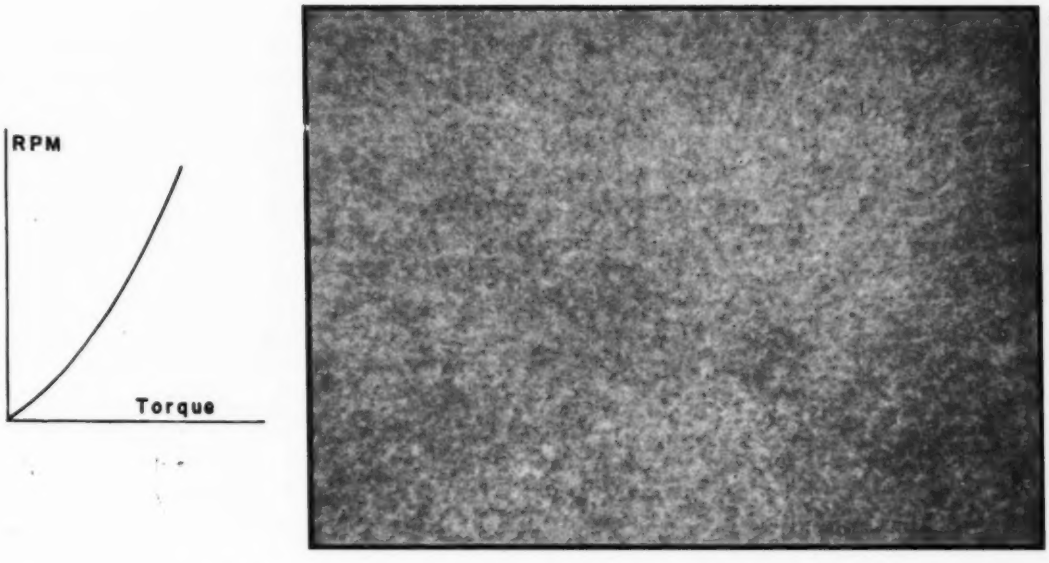


FIG. 13. A pseudoplastic suspension and its consistency curve. (1250×)

of flow produced by a known applied force, and then to be able to vary this force over a suitably wide range. When the rate of flow so obtained is plotted against the activating force, a consistency curve is the result. One of the easiest means for getting a consistency curve is by using a rotation viscometer of the Couetter type. The yield value and mobility can then be calculated from the Reiner[5] equation.

There are four fundamental types of consistency curves: Newtonian (Fig. 11), dilatant (Fig. 12), pseudoplastic (Fig. 13), and plastic (Fig. 14). Thixotropic materials give a so-called hysteresis loop (Fig. 15) when the up- and down-curves are plotted together.[6] This loop is the result of the thixotropic breakdown that the material undergoes when forced to flow.

Newtonians and pseudoplastics are usually clear liquids and show no structure under the microscope. Suspensions, however, sometimes give Newtonian and sometimes pseudoplastic curves and in such cases structure is visible. In both instances the pigment will be deflocculated. If this should not happen to be so, then it will be noticed that the pigment-vehicle ratio is so small that a continuous structure throughout the vehicle is not possible and, consequently, the pigment is not contributing anything toward the type of curve obtained (Fig. 16).

Dilatant materials are always crowded systems. The pigment will be found in Brownian motion and consequently deflocculated. A relatively slight change in the pigment-vehicle ratio can destroy dilatancy. The dilatancy curve is somewhat similar in form to a Newtonian turbulence curve. The experienced rheologist can usually tell which type he has by an inspection of the material itself.

Plastic suspensions are always found to be flocculated. It should be pointed out, however, that the force of flocculation can be recognized microscopically only by the effect it has on the particles. If its action is very weak, it often requires considerable skill on the part of the microscopist to demonstrate its existence. Time, here, is the important factor. When the force of flocculation is slight, a sufficient period must be allowed for the particles to contact before flocculation can be observed on the microscope slide. If the particles are spread too far apart and convection currents cease before the particles are brought together, it might be concluded that the force of flocculation is non-existent.

The simplest curve is the Newtonian. This curve shows that so long as streamline motion is maintained the velocity gradient is proportional to the activating force. This law also holds at the start of dilatant flow but as soon as the particles

are displaced from their position of minimum voids, this type of flow ceases and the resistance to flow increases at a more rapid rate. This can be accounted for by the fact that the pigment-vehicle ratio is so carefully adjusted that only enough vehicle is present to fill the voids and any increase in void volume (arising from flow) would create a condition of partial dryness; hence, the increase in the resistance to flow.[7] Flocculation prevents dilatancy by making it impossible for the particles to settle down to a position of minimum voids.[8]

The pseudoplastic curve indicates a deflocculated structure from the fact that it clearly starts at the origin of the force-flow diagram. As to the cause of the curvature one can only hazard a guess. The particles are probably appreciably elongated, and randomly arranged before flow commences. There is no indication that the particles form a connected *network*; i.e., there is no force of orientation holding the particles together. Streamline motion will then force the long axis of the particle parallel to the direction of flow. When this happens, the frictional resistance between adjacent layers changes in such a manner that a drop in the coefficient of viscosity results. Since it takes a definite force to hold the elongated particles in their aligned position—the heat energy tending to recreate a random distribution—a factor like yield value enters. It is quite possible that this quantity is directly related to the intercept of the tangent on the force axis. This has been referred to as the *pseudoplastic yield value*.[9]

To the industrial rheologist the plastic flow curve is perhaps the most interesting. Here the effects of structure, particle size, wetting, and pigment-vehicle ratio are in full evidence. It has been shown that the microscope reveals the existence of a definite force of flocculation. This force must be overcome before the flocculate can be sheared. The tendency to reflocculate is continuously present; consequently, a continuously externally applied force must be maintained above the force of flocculation, if continuous flow is to ensue. Any force less than this will produce zero shear. Therefore, if a hypothetical rotational viscometer could be operated where the distance between the bob and cup is so small that it could contain no more than two layers of the plastic, then the consistency curve obtained thereby would be a straight line giving an intercept on the force axis. The size of this intercept would depend on the force of flocculation, and the yield value would be directly proportional to it. The proportionality constant is a known function of the instrumental dimensions.[5]

Unfortunately, such an ideal viscometer does not exist, for the distance between the bob and cup must be made sufficiently large to hold a

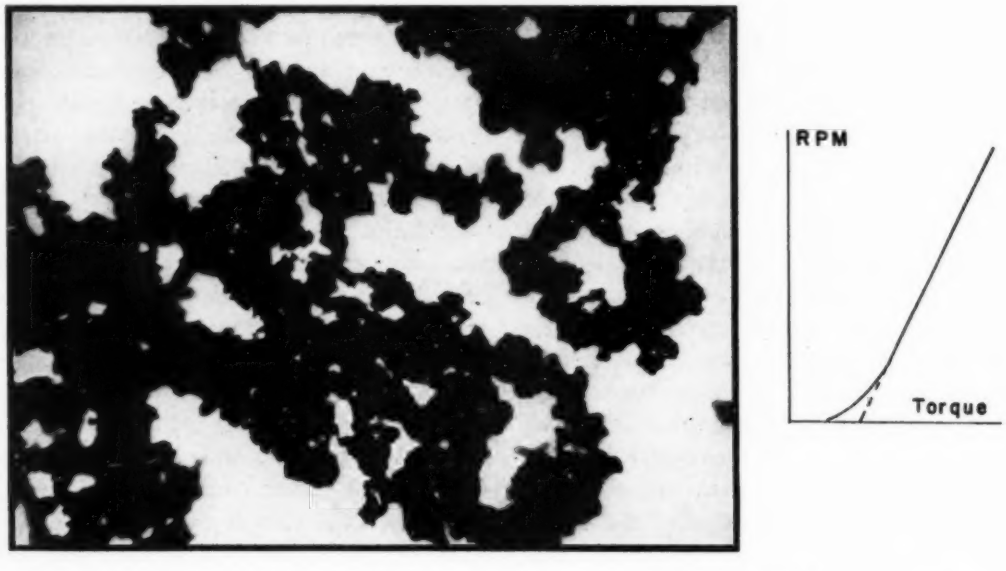


FIG. 14. A plastic suspension and its consistency curve. (400×)

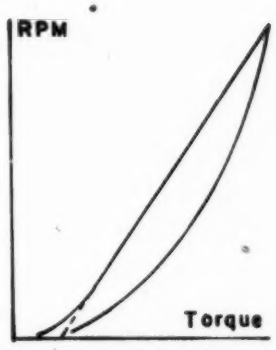


FIG. 15. A thixotropic hysteresis loop giving a graphic description of thixotropic breakdown.

practical amount of the substance being tested. This appreciable distance between bob and cup destroys the ideal linear relation at the lower end of the curve. The reason for this effect arises from the fact that the shearing force varies from the wall of the bob to the wall of the cup. If the yield value should be of such magnitude that it falls within these two limits, there will be two types of flow for that particular r.p.m. One will be solid plug flow on the side where the shearing force is less than the yield value, and on the other side, laminar flow will ensue. The ratio of plug to laminar flow changes with the r.p.m. At a certain critical value for the r.p.m. plug flow disappears, and from there upward only laminar flow exists. This region of laminar flow coincides with the "straight" part of the consistency curve. Below this part, the force-flow relationship becomes non-linear and the curve turns toward the origin.

There is a school of thought that believes that the turning of the lower end of the consistency curve toward the origin indicates the gradual disappearance of yield value under low shearing forces. This is difficult to understand because if the yield value disappears, the force of flocculation must become zero and a dispersed system would result. This the microscopist can see does not take place.

The force of flocculation involves both intensity and capacity. The more poorly wet the pigment is by the vehicle, the greater will be the intensity factor. The larger the specific surface of the pigment (i.e., the smaller the d_3 diameter) the greater will be the capacity factor. Capacity also depends on the pigment-vehicle ratio, increasing as this ratio becomes greater. It is necessary to bear these facts in mind when comparing the microscopy of a suspension with its consistency curve. A high yield value might be due to a strong flocculating force. If, however, microscopical examination reveals evidence of only weak flocculation, then one must look for either small particle size or a high pigment-vehicle ratio. A microscopical examination will readily show which condition exists.

Yield value is calculated from the intercept obtained by extrapolating the straight part of the consistency curve to the force axis. The tangent of the angle that this extrapolated curve makes with the force axis is directly proportional to the *coefficient of mobility*. The proportionality constant depends on the dimensions of the viscometer and is given in the Reiner equation. The writer[6,10] has suggested that the reciprocal of mobility be called *plastic viscosity* because of its analogy to the viscosity of liquids. Plastic viscosity is a constant and in this respect differs from the apparent viscosity of a plastic material.

The plastic viscosity of a pigment-vehicle suspension is always greater than the viscosity of the vehicle. Increasing the pigment content, decreasing the particle size, and lowering the wettability of the pigment all increase the plastic

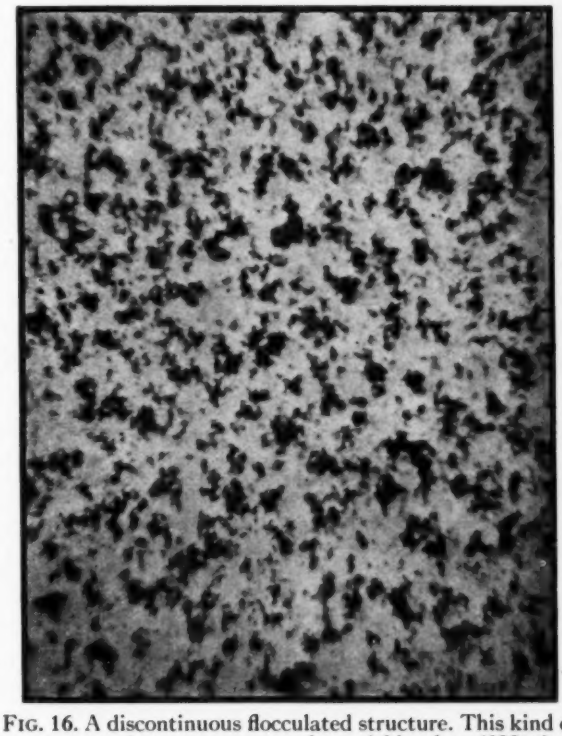


FIG. 16. A discontinuous flocculated structure. This kind of structure is too open to produce yield value. (300×)

viscosity. Wetting agents, if they actually increase wetting, lower both yield value and plastic viscosity. A material might act, however, as a wetting agent in one system and act in exactly the reverse manner in another. In this latter case both the yield value and plastic viscosity would be increased.

ACKNOWLEDGMENT

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Calendar of Meetings

September

29–Oct. 1 Technical Association of Pulp and Paper Industry, Boston, Massachusetts

October

5– 9 National Safety Council, Chicago, Illinois
12–14 American Society of Mechanical Engineers, Rochester, New York
12–16 American Welding Society, Detroit, Michigan
12–16 American Society for Metals, Detroit, Michigan
19–24 American Society for Metals, Chicago, Illinois
19–24 American Society for Metals, Cleveland, Ohio
30–31 Optical Society of America, New York, New York
30–31 Society of Rheology, New York, New York
30–31 American Mathematical Society, New York, New York

November

7 American Physical Society, New York State Section, Albany, New York
16–18 American Institute of Chemical Engineers, Cincinnati, Ohio
27–28 American Physical Society, Chicago, Illinois
27–28 American Mathematical Society, Notre Dame, Indiana
30–Dec. 4 American Society of Mechanical Engineers, New York, New York

December

27–Jan. 1 American Society of Naturalists, New York, New York
28–31 American Physical Society, New York, New York
28–Jan. 2 American Association for the Advancement of Science, New York, New York
28–Jan. 2 American Standards Association, New York, New York
29–31 Geological Society of America, Ottawa, Canada

The Mechanical Properties of Glass

By F. W. Preston

The Preston Laboratories, Butler, Pennsylvania

THE manager of an American publishing firm once decided that authors were not submitting manuscripts fast enough, and his business was languishing for material to publish. He decided to take the initiative, and figuring that elephants were interesting to the public, wrote to several authorities on the subject. An Englishman submitted a manuscript entitled "Elephants I have shot, with some comments on the ivory trade." A Frenchman submitted a perfumed document entitled, "Samson, or the amours of an elephant." The German invitee produced a ten volume work entitled, "Elephants in health and disease; their life, death, and metaphysical significance, with an account of the giraffe and rhinoceros."

Some twenty years ago, an American college group pulled off a stunt in the form of a lecture on low temperatures, entitled "The moral significance of liquid air," in which one of the students disguised as a very hairy and woolly Bolshevik, was introduced to the audience and requested to "Pulloffski the Stuntovitch."

A lecture on the mechanical properties of glass and glassware a few years ago might have been regarded as in the same category, for it might be held that the mechanical significance of glass was on a par with the metaphysical significance of elephants or the moral significance of liquid air; or that the mechanical properties of glass could be described in exactly the same words as the famous treatise on the snakes of Ireland, *viz.*, "There are none."

Normally, glass is thought of as being valuable and significant for its optical properties, chiefly for its transparency. The initiated think of glass as having value for its chemical durability, its resistance to corrosion, or its electrical insulation. And they are all correct. Yet the largest single piece of glass ever made, and by far the most valuable, *viz.*, the 200-inch mirror for Mount Palomar, is made of glass, not for any optical property, not for transparency, not for electrical resistivity, but for its mechanical properties. In this case we are concerned with permanence of shape, freedom from "creep," freedom from elastic hysteresis, freedom from warping and from thermal distortion. For in that mirror, the silver or aluminum is on the front face, not the back one, and the light never passes through the glass. The glass is a purely mechanical support for the almost infinitesimally thin mirror. We use glass in this case, not because it is transparent, but because its general rigidity and permanence of shape are better than steel or concrete.

As a matter of fact, glass is the best material we have in which to study the mechanical properties of matter. It introduces many simplifications as compared with metals, wood, etc.; or, better expressed, it avoids the complications that these latter introduce. An understanding of the mechanical properties of glass may not be sufficient to enable us to grasp the complex phenomena in steel or aluminum; but it is a good introduction thereto, and from the point of view of the physicist, as distinct from the engineer, a necessary introduction.

BRITTLENESS

The thing that distinguishes glass from most other materials is its excessive brittleness. This brittleness is of a totally different order from the so-called brittleness of cast iron, which is often regarded as among the poorest, weakest, and least satisfactory of structural metals. No one will deny, however, that the behavior of cast iron is angelic, in respect to brittleness, as compared with the behavior of glass. The concept of brittleness is of itself a complex one, not easily defined in rigorous terms. The fundamental physical factors have been discussed by the present writer.[1] They involve the simultaneous presence of a relatively high elasticity, a fair to high tensile strength, and a complete absence of plasticity or of ability to store energy or to dissipate it by plastic flow. To some of these points we shall return later.

COMPARISON WITH METALS

Certain mechanical properties of glass are very simple and correspondingly uninteresting. Maybe we had better deal with some of these first.

Glass has about the density of aluminum, and about one-third the density of steel.

It has an elasticity about that of aluminum or brass, and about one-third that of steel. That is, it is only one-third as stiff as steel.

It follows that the velocity of sound in glass should be about equal to that in some of our most familiar metals, *viz.*, steel and aluminum.

Poisson's ratio in glass appears to be generally lower than in the metals, but no particular interest has appeared, up to date, to attach to this fact.

The foregoing remarks would seem to indicate that in a broad sense, glass lends itself to being compared with our ordinary metals of construction; in fact it challenges that comparison. It does not challenge comparison with wood, rubber, or plastics.

In numerical values, the density of a typical glass is about 2.5 grams per cc or 0.09 lb. per cubic inch, or 150 lb. per cubic foot. Glass can be made considerably heavier than this, but the amount that *is* so made is an infinitesimal fraction of one percent.

Young's modulus is about 10,000,000 lb./sq.in. ("psi") compared with 30,000,000 for steel.

Poisson's ratio is usually about $\frac{1}{4}$ but is reported as low as $\frac{1}{8}$ at times. Most metals run above $\frac{1}{4}$ and often near $\frac{1}{3}$.

The velocity of sound in glass is about three miles per second.[2, 26]

GLASS AS A VISCOUS SUBSTANCE

Now from the point of view of the physical chemist, glass is an undercooled liquid. This is a good deal of a catch phrase. All that is meant by it, is that it is below its crystallizing temperature, but hasn't crystallized. It doesn't mean that it is a liquid at all. It merely means that it is "undercooled."

Nonetheless, the dog has been given a bad name, and he might as well be hanged. He has been called a liquid and the characteristic of a liquid is that it has constant volume (at constant temperature) but no fixed shape, except that of its container. Its characteristic is its mobility, or its fluidity. Now in the precise language of physics, fluidity is the reciprocal of viscosity and nothing else. Hence the characteristic feature of a liquid is its viscosity, and everybody knows what that is. Mathematically it is the (steady) shearing stress that has to be applied to produce unit rate of (shearing) flow; or more simply, it is (steady) shear stress/rate of flow produced thereby.

The assumption in this definition, which is never explicitly stated, is that no change is produced in the liquid except the flow, that is, the movement. Geologists and some physicists have not always been meticulous on this point, and in dealing with high viscosities (say above 10^{14} poises) have produced other changes, such as twinning in marble or lattice destruction ("cold work") in metals, so that the last state of the substance is different from, and worse than, the first. Nonetheless, they have divided shear stress by shear strain and reported it as a viscosity, whereas an honest experiment on viscosity, when completed, must leave the substance in a condition indistinguishable from its original state. Cream must not turn into butter during the experiment.

Returning now to the glass, it is to be observed that if we once call it an undercooled liquid, we make the mental assumption that it can flow and that it can be defined by its viscosity. We know from earliest infancy, that the viscosity of glass at room temperature must be very high, entirely out of line with the viscosity of other undercooled liquids, such as undercooled water. We do not expect to stick a stirring rod into a lump of cold glass, and cause it to crystallize instantly. We do not expect to be able to stir it at all.

But having called it a liquid, we do expect it to flow, and so we have stories of old cathedral windows being thicker at the bottom of the pane than at the top. The assumption is made that originally they were equally thick all over, and that in the course of a few hundred years, under the trifling stress due to their own weight, they have flowed down like molasses. The possibility that they were originally very far from equally thick all over has to be considered.

At high temperatures, above about 1000°F, the viscosity of glass can be measured readily. If

the glass does not devitrify during the experiment, either because we are working above the liquidus temperature, or because the composition is such that crystallization is very slow, we can measure the viscosity by a variety of means, preferably using different techniques in different temperature ranges, and thereafter make a plot of viscosity against temperature. A number of precautions must be observed, especially in the lower temperature ranges, to make sure that a steady state has been attained, and that we are dealing with "stabilized" glass—that is, a glass whose atomic or molecular or physical "constitution" is actually the constitution appropriate to the temperature at which we are working. In the very lowest temperature ranges this is impossible. The glass never reaches equilibrium constitution. But in the higher ranges it reaches it promptly.[3]

It is found that glass is a truly viscous substance in the temperature range at which it is practicable to experiment. Rate of flow is strictly proportional to the applied stress, which is the definition of a perfect liquid. The quotient is the coefficient of viscosity η.

Since η is usually given in c.g.s. units, it is convenient to measure temperature in "absolute centigrade" or "Kelvin" units. Call this temperature T.

Then both on the basis of quantum theory and on the basis of experience, it will be found convenient to plot the logarithm of the viscosity against the reciprocal of the absolute temperature, i.e., to plot log η as ordinate against $(1/T)$ as abscissa. In that way we have a good chance to get a straight line, which is what we generally admire in a graph.

Such a plot is given in Fig. 1.[4] It is obviously a straight line over a considerable temperature range, and there is every reason to believe that it would continue as a straight line to lower temperatures, if the stabilized constitution appropriate to these temperatures could be obtained. By stabilized constitution we do not mean that below the liquidus it should be partly crystallized, and that below the solidus it should be completely crystallized. We have been coming in recent years to a concept of a non-crystalline constitution, an association of atoms and molecules in a disordered condition, which is somehow appropriate to the particular temperature, though as compared with a crystallized condition it may be thermodynamically unstable. The physical picture of the disarray, the social organization of the mob, has been painted somewhat convincingly by Warren;[5] the thermodynamical iniquity of it has been discussed by Morey;[6] the existence of variable states, that is, departures from the "appropriate" state, was

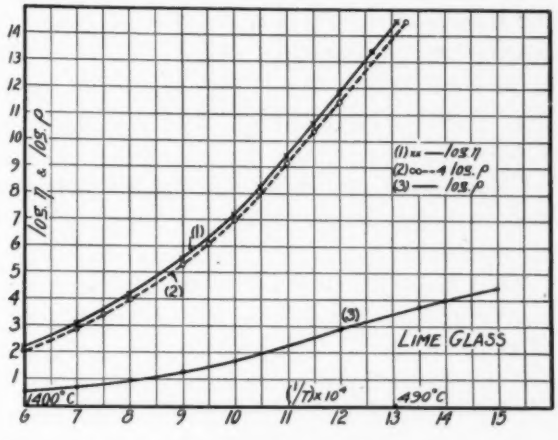

FIG. 1. Viscosity of glass as a function of temperature. From J. T. Littleton, "Critical temperatures in silicate glasses," Ind. Eng. Chem. **25**, 788 *et seq.* (1933).

first indicated by A. Q. Tool;[7] the effect of such "frozen-in" constitutions has been discussed in many papers by Littleton[8] and his associates.

Returning now to the graph, we can hardly resist the temptation to extrapolate the line to room temperature. Suppose we could somehow get a glass that had been stabilized at 20°C or thereabouts, how viscous would it be? Apparently the viscosity would be around 10^{60} or 10^{70} poises. This figure conveys no meaning to us because it is something entirely outside our experience, or even our imagination. The present writer discussed this several years ago in a note on viscosities of the order of 10^{70} poises. In a somewhat paraphrased form, this is repeated below:

"The velocity of light is 186,000 miles a second or 3×10^{10} cm/sec.

"The oldest known rocks on this earth are some 2000 million years old, or 6.3×10^{16} seconds. In this time light would travel 1.9×10^{27} centimeters. That is, 2000 million light years represent this number of centimeters. It is not certain how large the universe is and it may not hold a straight line as long as this. Suppose, however,

that at the dawn of creation the universe had been wrapped round with a glass fiber of this length, and that for two billion years the pressure of the expanding universe had maintained a stress in the fiber of 5000 lb./sq.in. or 3.5×10^8 dynes/cm. This may be a greater stress than the fiber could support for so long without breaking, but let us suppose it could and did support it. Let us suppose further that the temperature of the glass fiber did not sink to that of outer space, but was held at about 20°C, where the "viscosity" is, as we imagine, 10^{70} poises. (If it got colder, the "viscosity" would rise, becoming infinite at absolute zero.)

"How much would this immensely long fiber have stretched viscously in this immense length of time?

"The answer is 1.4×10^{-18} centimeter, or much less than one-thousandth part of the diameter of an electron.

"Two deductions follow from this:

"(1) Viscosities of this order have no physical meaning in mechanical terms, but only as probability functions.

"(2) The attempt to induce a permanent set of measurable amount in a glass rod one yard long at room temperature in the course of a year or two is not likely to lead to positive results. The phenomena discovered by Mr. Spencer are thus almost certainly not phenomena of viscous flow in the ordinary sense of the word; they must be something totally different, and possibly much more significant."[9]

Obviously when we start talking about all eternity, all infinity, and a fraction of the diameter of an electron, we are not talking kitchen physics, the physics where the concept of viscosity belongs, as in the stirring of batter or the making of fudge. We have taken the concept of viscosity into fields where it does not belong; we should have to pass outside of time and space before we could give it a meaning analogous to the original concept. In other words, in our present universe there is no such thing as a viscosity of 10^{70} poises. It is not merely experimentally unrealizable, but is naturally meaningless. This lack of physical meaning may be correlated with the fact that it is unthinkable that the "appropriate constitution" could be attained by any schedule of cooling a piece of glass, even if we had several billion years in which to do it.

Thus all glass is clearly, at room temperature, in some other condition than the "appropriate" one. It has a "frozen-in" constitution, possibly appropriate to some other, higher, temperature, or possibly it has a mixture of constitutions, appropriate in part to several higher temperatures.

Littleton,[10] seeing that viscosity could not be measured anywhere within several hundred degrees of room temperature, approached the subject from the angle of electrical conductivity, which can be measured to much lower temperatures, and by considering the parallel course of electrical conductivity and viscosity, and how they vary with temperature, reached the conclusion that at room temperature a fairly typical soda-lime glass should have a viscosity of about 10^{63}. At an earlier date a lower viscosity, of the order of 10^{27} or 10^{30}, was suggested as a minimum viscosity for glass at room temperature,[11] but even a viscosity of 10^{30}, though an infinitesimal fraction of 10^{70}, is still far outside human experience, and it is not certain that it has any physical meaning. In fact, if we go beyond a viscosity of about 10^{14}, or at the most 10^{17}, it is not certain that we are dealing with matter at all. Viscosity in practice, like atomic weights, has an upper limit, beyond which there isn't any.

To test the question whether glass really was a viscous substance at room temperature, Rayleigh[12] loaded a rod about a meter long, supported at the ends in a horizontal position, with a central load, and left it there for seven years. When the load was taken off, the rod apparently was not definitely bent.

C. D. Spencer[13] thereupon carried the investigation further. He wound glass fibers around tubes about 2 cm in diameter and stored them at temperatures somewhat above room temperature, above an industrial furnace. When he finally cut the fibers free, they were bowed to a radius of about 60 cm. This would seem to indicate viscous flow, but Spencer floated his bent fibers on mercury, and found that they straightened out, rapidly at first and more slowly later. This is inconsistent with the distortion being due to viscous flow. The fibers perhaps merely had the cramps, through being doubled up so long. They recovered comparatively rapidly,

in spite of the fact that fibers have an abnormally light "constitution," a low density, and low viscosity, and in spite of the fact that viscous flow had been further encouraged by keeping them at temperatures well above room temperature.

At the moment, I am not sure that we know whether this temporary condition of "cramps" is due to a genuine elastic hysteresis, or to a polarization of the surface of the glass by the surrounding atmosphere.

The dangers, or the inadequacy, of thinking of glass as a viscous fluid while we think of steel as a true elastic solid, merely because it is crystalline, are pointed out by Jeffreys, who says in substance that the most perfect elastic substance is vitreous silica.[14] "Since the recognition of the resemblances between liquids and glasses, few references to the latter have been considered complete without the statement that a glass is a supercooled liquid. This statement is a dangerous half-truth. The identity can be admitted only if it is agreed to ignore the differences; the chief difference being in this case that liquids have no rigidity, whereas the rigidities of glasses are not only finite but comparable with those of crystals. If, with some authors, we regard *complete* recovery of the original shape after deformation and release as the characteristic property of a solid, then as a matter of experiment the most typical solid known is vitreous silica."

STRENGTH

Now flow is a response to shearing stresses, and presupposes a finite viscosity; finite, not merely in the mathematical sense, but in the sense of falling within the realm of physics, of real substances. When the viscosity becomes infinite, which in the real world seems to mean exceeding something like 10^{15} poises, this response is no longer available. The material is now elastic, and in the case of glass, brittle.

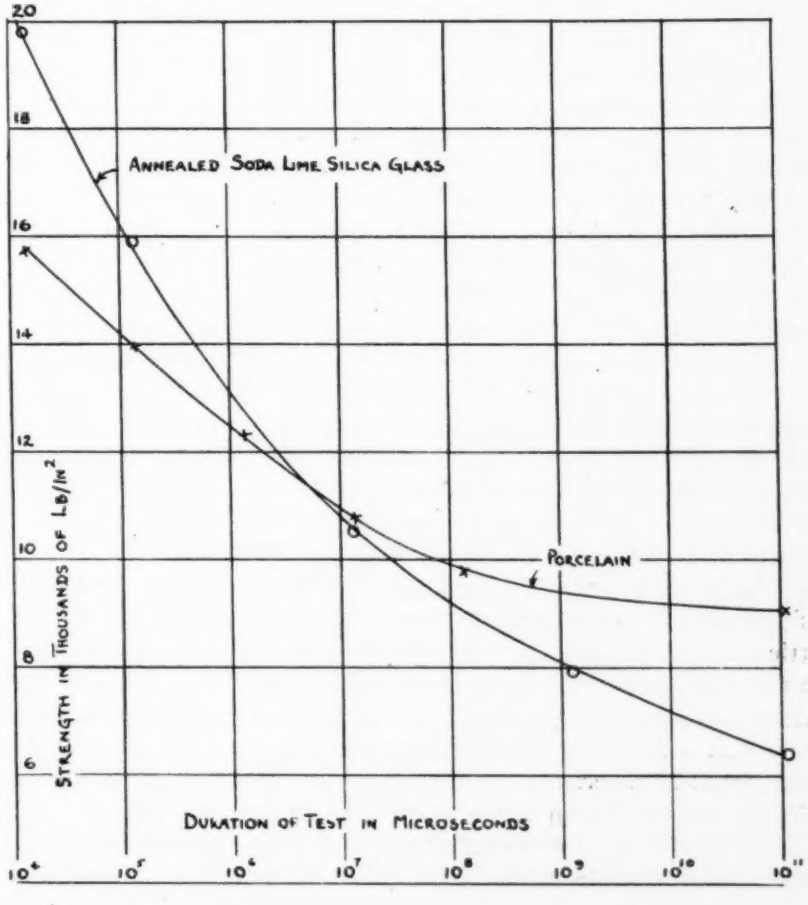

FIG. 2. Fatigue of glass and porcelain under steady loads. Curves obtained by Theodore C. Baker under sponsorship of Hartford-Empire Company, at Preston Laboratories, about 1939.

It can stretch in response to tension, contract in response to compression, distort in response to shear, but it cannot flow. Under certain circumstances it can break, and this is the characteristic feature of glass, the thing that causes it to be most distrusted. Under any ordinary circumstances, glass breaks only in response to a tensile stress, and the fracture is at right angles to the maximum tension.

Now the numerical value of the tension that produces failure, or as we normally express it, "the strength of glass," is a very elusive quantity.

Theoretically, it would seem that glass should have a strength of several million pounds per square inch, so that it should stretch to nearly double its length before it breaks. The heat of combustion of silica with oxygen is very high, and to rupture this bond by simple stress at room temperature ought to take a lot of stretching, and a lot of elastic energy.

The observed values of strength in very fine fibers run up above a million pounds per square inch,[15] but the values found in normal testing of rods, laths, and window panes are usually no more than one percent of this, that is, around 10,000 lb./sq.in. Moreover, if the load is left on for any great length of time, it is not safe to figure on a strength of more than 3000 lb./sq.in., under what might be called normal conditions, and in certain abnormal conditions it is even less. Thus glass might be said to have normally not more than one thousandth part of the strength that is to be expected of it.

FATIGUE

Glass will carry a heavier load for a few seconds than it will carry for a minute; it will carry a heavier load for a minute than it will carry for an hour; and it will carry a heavier load for an hour than it will carry for a day. This fact has been known, in a rather vague way, to the scientific world for a generation or more,[16] but very little attention was paid to it until the last decade. In fact it might be said that the scientific world rather completely ignored the fact, although there were a few glass manufacturers who knew from practical experience that the fact was important, and based their testing procedures on it.

L. T. Sherwood[17] observed that panes of glass under load might stand the additional momentary load of heavy blasting in their neighborhood, which shook the ground and rattled the windows, and yet might break a few hours later at a time of perfect quiet.

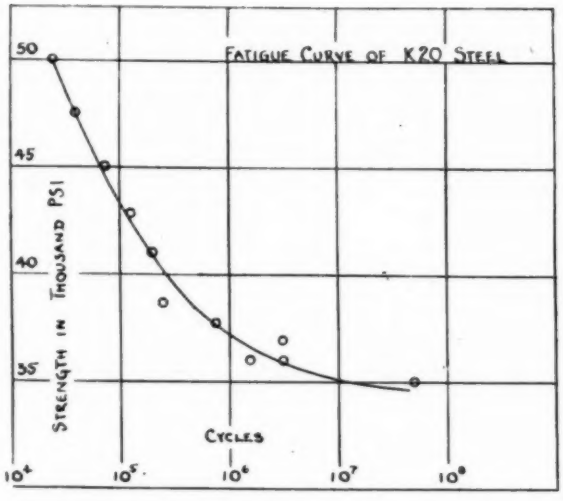

FIG. 3. Fatigue of steel under repeated stressings, from *Prevention of Failure of Metal under Repeated Stress* (Batelle Memorial Institute Monograph) (John Wiley and Sons, Inc., 1941), Fig. 72, p. 46.

In Fig. 2 we give what we believe to be the longest range of time values of stress yet obtained. The specimens used were rods, about $\frac{1}{4}''$ diameter, carefully chosen to meet statistical requirements of sampling, enough samples being used for each point on the curve to give a sound average value. The time was controlled with precision, the temperature did not vary greatly, and the humidity and certain other factors were under much closer control than usual.

Special apparatus was designed for the testing, involving electrical loading for the short time tests. This made it possible to apply the load in 1/1000 of a second, hold it steady for 1/100 of a second, and take it off in 1/1000 of a second. Thus the curve goes much further toward the short time end than in other published results. The manner of plotting, with average breaking strength as ordinate and log (time) as abscissa has become general. Some previous curves, through faulty plotting or through inadequate time range or both, represent the curve as a straight line. This it definitely is not. The extension of the curve to the long time end is difficult, because life is too short. When the next point of interest involves a time say 100 or 1000 times as

long, and must be determined on a comparatively large number of specimens to get a good statistical average, it is difficult to maintain constant conditions; and to get two such points would carry the experiment into our great-great-grandchildren's days. Probably the curve has now been extended as far both ways as is practicable, but up to date the theoretical equation of the curve remains unknown.

It should be clearly understood that the decline in strength with the passage of time does not involve increasing strain or increasing deflection. The full deflection or extension is obtained immediately on application of the load; or if not, the additional deflection that occurs later is extremely trifling in amount.[18,19]

COMPARISON WITH STEEL

The term "fatigue" as applied to glass has come to mean decline of strength under a steady static load. This is not the meaning of the same term when we refer to metals. In the case of steel, and other metals for that matter, it has been found that the metal will stand up much better under a steady load than under a varying one, like a vibration or a pulsating load such as springs most commonly support. The same thing may be true of glass, but no work on the point seems to be on record. In the case of glass our data relate principally, or entirely, to fatigue under static load: in the case of metals, the data relate principally to the decline of strength as the load is applied more and more times. The data, for metals, are customarily plotted on the same basis as we use for glass, *viz.*, with stress plotted linearly as ordinate, and number of repetitions plotted logarithmically as abscissa.

When thus plotted, the curves for glass and steel are remarkably similar, as may be seen by comparing Fig. 2 (for glass) with Fig. 3 (for steel).[20] However, there do not appear to be published any data for steel that cover so wide a range of abscissae as we have provided for glass.

It should be observed further that not only are the curves similar, but the physical behavior of the materials is similar. Under "fatigue" conditions, even ductile metals break with a brittle, tensile, fracture like glass,[21] whereas under a heavy static load they pull out and neck down, exhibiting much plastic flow.

VARIATION OF STRENGTH WITH TEMPERATURE

The strength of glass is a mysterious quantity, and it is not clear upon what factors it depends. One of the best ways to investigate a phenomenon whose very nature is obscure, is to investigate its variation with temperature. That may give us some clues as to what we are dealing with.

In Fig. 4 we give a plot of strength against temperature, from the range of liquid nitrogen to the approach of the softening temperature. This happens to be a curve from our own laboratory, but a comparable curve has been given earlier by Smekal.[22] We have preferred to use our own curve, because it was obtained in a somewhat different manner, and perhaps with more of the relevant factors under control; but we are tolerably sure that in the lower temperature ranges, the equilibrium conditions for strength were not attained. The temperature was steady and accurate, but the physico-chemical equilibrium of the glass surfaces with the surrounding atmosphere had probably been "frozen" at some higher fictive temperature and the strengths obtained, though high, are still not high enough.

It will be observed that glass when it is really cold, or really hot, is much stronger than at room temperature. There is a minimum strength at perhaps 200°C. On the face of things this is very significant.

COMPARISON WITH STEEL

This minimum strength of glass at temperatures somewhat above room temperature is in striking contrast with steel, which generally has a maximum strength in this region (Fig. 4). The data, relating to the temperature coefficient of strength in metals, are, however, not very satisfactory, and may not be directly comparable with the experiments on glass. They do suggest, however, that the failure of metals, under the conditions of such experiments as we have, is not conditioned by the same factors as cause the failure of glass.

CRACKS IN GLASS

In 1941, in the United States alone, there were made some ten billion bottles. At the end of the year, there were probably more bottles in existence than at the beginning, but a very large pro-

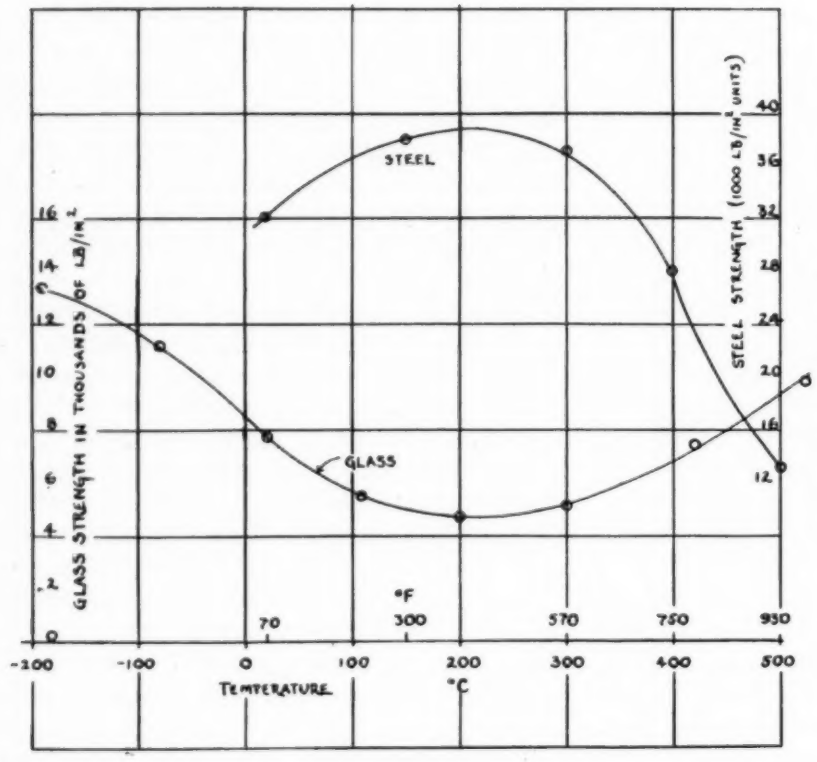

FIG. 4. Strength of glass and steel as a function of temperature. The data on glass are results of Bernard Vonnegut, under sponsorship of Hartford-Empire Company, at Preston Laboratories, 1940. They agree with earlier results of Smekal, and apparently disagree with recent results of Jones and Turner [J. Soc. Glass Tech. **26**, 35 (1942)]. The data on steel are taken from the Battelle Monograph above cited.

portion of those that had been made were already broken; and in addition a few billion of earlier vintages were broken that year. Besides bottles, all sorts of other glassware were made, and much of it was broken. Untold billions of cracks were made in that year alone, and comparable billions were made in preceding years. Yet from the beginning of time to its end, no two cracked surfaces of glass will fit each other, unless originally they were part of the same piece. Cracks are as distinctive as fingerprints. On their faces you may see, except in rare instances, fine markings whose nature has been discussed by the present writer[23] in several papers.

Cracks in glass and in other brittle substances seem to be a response to tension, to open at right angles to the maximum tension, and to extend in such a manner that they are always advancing at right angles to the maximum tension at the head of the fissure. Since the extension of the crack is itself a cause of redistributing the stress, it is not possible to predict the course of the crack solely from a consideration of the stress system in existence before the crack starts; the redistribution as the crack progresses has also to be taken into account.[24] Bridgman is of the opinion that cracks do not necessarily demand a tension to call them into existence, but that under some conditions they are best understood as a response to minimum energy requirements.[25] After repeating some of Bridgman's experiments, we have been unable to satisfy ourselves that his point is proved, and prefer to leave it open. In any case, under normal conditions, that is, excluding the physics of high pressure, the fracture of glass is a response to tension, and to that alone among stresses. There is no evidence that glass can be broken in compression or in shear, except insofar as these produce accidental, or incidental, tensions.

Now the important thing about cracks is that they must be propagated. They do not originate all over the final fracture-surface, but at one tiny spot, and from thence are propagated out to the rest of the area. This fact, and the fact that telltale marks or "fingerprints" of the process are left on the surface, provides the groundwork for the subject of Fracture Diagnosis, which in the last decade has become an important minor branch of physical science.

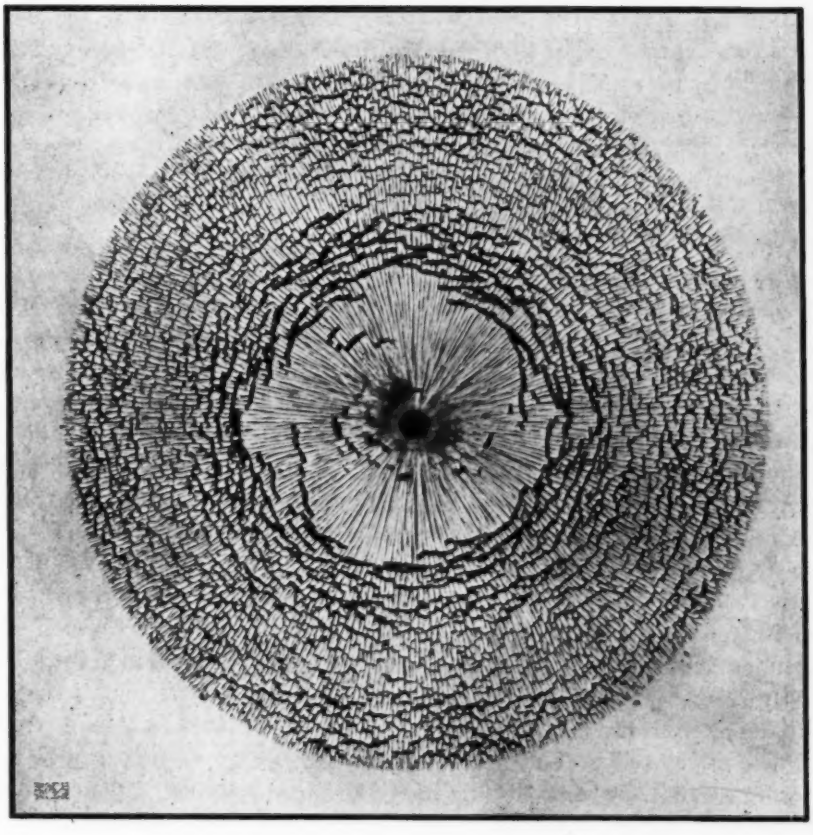

FIG. 5. Propagation of cracks in glass at limiting velocity of about 3 miles per second. F. E. Barstow and H. E. Edgerton, "Glass fracture velocity," J. Am. Ceram. Soc. 22, p. 306.

In the course of propagation, the crack does not necessarily remain a single surface, but may fork and become a highly ramifying system of fractures. In fact this is the usual result. Otherwise a broken bottle would be always in two pieces at most, and not in a lot of fragments.

VELOCITY OF CRACK PROPAGATION

If cracks are propagated, they must spread with a finite velocity. That velocity may be very high, however, and highly specialized techniques are necessary to deal with the maximum velocity. It might be expected that this velocity would be the velocity of sound in glass, but this appears not to be the case; the maximum velocity is apparently only one-third the velocity of sound.[26] Schardin and Struth offer some evidence that the maximum velocity is the only velocity, that if the crack does not go at full speed, it does not go at all. The evidence on this point, however, may be held to be short of full conviction, and a satisfactory proof that no lower velocity is possible may become involved in a metaphysical argument as to how finely *time* can be divided. It is certain that cracks can and do extend at a rate, which measured over seconds or over a few tenths of a second, is an infinitesimal fraction of the maximum speed. It is not easy, however, to disprove the contention that the seemingly steady motion is made up of a surge forward lasting a millionth of a microsecond, followed by a dead stop for half a microsecond. This view, of course, runs into the trouble, in the long run, that the final structure of matter is discontinuous, and we cannot conceive of a crack being propagated less than an atomic diameter or so, or say a linear distance of 10^{-8} inch.

Figure 5 shows a crack system being propagated through a sheet of hardened plate glass, which has been struck near the center. The remarkable circularity of the rosette outline shows how uniform the speed of propagation is, though enormous numbers of cracks are involved.

The speed of propagation in a soda-lime-silica plate glass is given by Schardin and Struth[26] as approximately 1550 meters/sec., or 5080 ft./sec.,

and this figure is confirmed by Edgerton and Barstow,[2] who report 5040 ft./sec. In fused silica glass the speed is higher, 7220 ft./sec.[26]

These velocities were measured at room temperature. The temperature coefficient of the effect is apparently not known.

EFFECT OF SURFACE ABRASIONS

The ordinary concept of a scratch on glass as a furrow or crevice is not very accurate. A typical scratch on glass does not remove any material, and does not produce plastic flow, unless extreme local temperatures are reached. Oftentimes the nature of the scratch or even its existence, cannot be determined without subsequent etching. It is then seen to consist of a series of transverse cracks, crescentic in form, which together form a "chatter-sleek"[27,28] or ladder. The path of the abrasive is not a crack: the individual rungs of the ladder *are* cracks. They have, under some circumstances, an extraordinary weakening effect on the glass, particularly against impacts administered from the opposite side of the glass.

These chatter-crescents represent the effect of intermittent seizing and slipping of the abrasive on the glass surface. The abrasive does not have to be sharp[27] or even hard.[28] The most important factor in producing such abrasions is often the cleanness of the surface. If the surfaces are clean, they seize very easily[29] and bite on one another like a bow on a fiddle string. Contaminated surfaces require much greater pressures to do any damage.

CRACKS AS RE-ENTRANT ANGLES ("NOTCH EFFECT")

In all materials, re-entrant angles act as stress concentrators and greatly weaken the material. A crack is an extreme example of a re-entrant angle, exceedingly sharp at the apex. This subject is by now well studied, though it does not always get the attention it should, even from structural and mechanical engineers. In the glass field, some of the most interesting published comments are those of Spencer, on the internal frosting of electric lamp bulbs.[30] The frosting is done by a strong hydrofluoric acid solution, which tends to coat the inner surface with angular crystals, between which deep re-entrant crevices are etched into the glass. Although these crevices are by no means so sharp as cracks, they are nonetheless severe stress-concentrators, and the bulb becomes extremely fragile against external rappings. Spencer therefore followed the etching process with a "fortifying" treatment, which consisted simply of etching with a dilute solution, whose effect is to round out the crevices.

Now any ordinary piece of glass is likely to

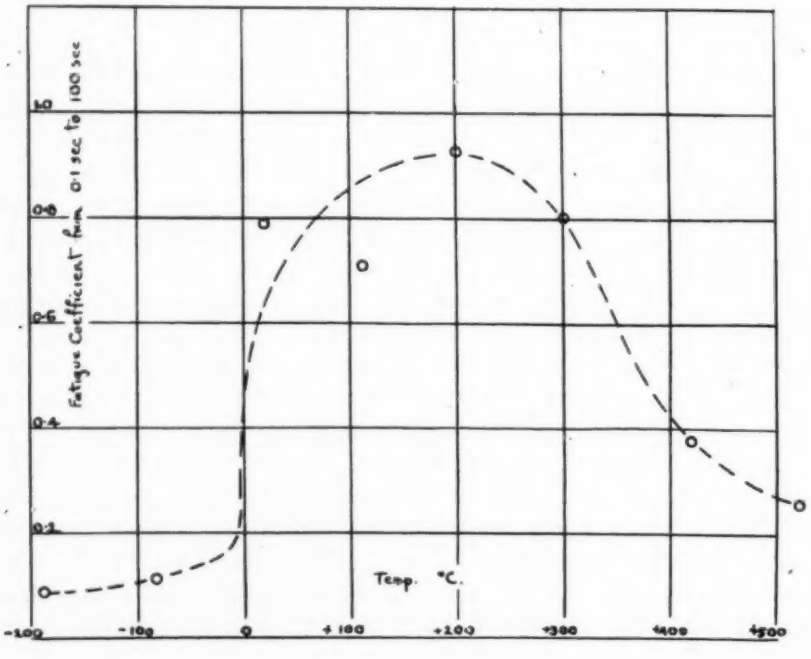

FIG. 6. Fatigue of glass as a function of temperature based on data of B. Vonnegut, Hartford-Empire Company, research fellow at Preston Laboratories.

acquire surface abrasions, and thus ordinary tests for strength are made upon glass which is already substantially damaged. The "strength" that we find is simply the residual strength, and what we really measure is not how strong the glass is, but how nearly broken it is already.

One way to get abnormally high values for strength, is to "fortify" the surface, etching it deeply with a dilute solution of hydrofluoric acid, thus rounding out the crevices. Then, being careful not to injure, in fact not to touch, any part of the specimen that will be called on to sustain a heavy tensile stress, we can set the thing up for test, and find it probably ten or twenty times as strong as an unfortified specimen. Dr. Littleton has reported substantial beams of glass to be stronger than nickel steel under these conditions.

There is nothing very mysterious about the notch effect. A tensile fracture is a tear or rip, and everyone knows how to tear a sheet of paper or a piece of cloth in two. It isn't easy till you have started a snip or cut at one edge. To start a tear in the middle of a sheet of paper is quite an undertaking. We have to begin by making some stress-concentrating nick, and it is much more easily done at the edge than elsewhere. The same thing is true of metals, and of glass. Fatigue failure in metal nearly always begins at the surface, or the equivalent of a surface, and so do cracks in glass. Save the surface and you save all. This is why we polish airplane propellers, and having polished them, etch them at intervals as a regular maintenance procedure.

But the spontaneous decrease of strength that occurs in glass by the mere lapse of time is not so easily understood. It seems to have been first noted by Griffith,[31] who observed that freshly drawn fibers had a phenomenal strength, but that merely touching them with clean fingers destroyed most of it, and merely waiting without touching, had a highly demoralizing effect. Even more remarkable decreases of strength from seemingly inadequate causes have been observed by other experimenters.

EFFECT OF MOISTURE

A very significant observation was made by Milligan,[32] that certain liquids, notably water, reduced substantially the strength of cracked glass. Since all glass is normally more or less cracked, the observation is necessarily somewhat more universal than Milligan originally thought. Glass spontaneously adsorbs a moisture film, which breaks up, apparently, some of the strong silica bondings in the surface layers of the glass, and produces a weakened surface structure analogous to a slightly cracked one. If this surface film is driven off, any ordinary specimen of glass (at room temperature) becomes some three times as strong. This is true of pure silica ("quartz") glass as well as of typical commercial glasses.

The effect of moisture on the surface is very pronounced at room temperature, but it is even more so at autoclave temperatures. The phenomena are a little complex, and this is not the place to discuss them, but the guilty finger points unmistakably at the adsorbed moisture film as one of the major causes of the misbehavior of glass.

The ordinary variations of weather, in this part of the world, are sufficient to cause variations of several percent in strength from day to day. The difference between saturated conditions, i.e., obvious wet upon the surface, and a perfunctory drying in warm air, may be as much as 40 percent. Drying in a vacuum readily produces a doubling or trebling of strength. Up to date, however, we have not succeeded in producing such large increases of strength as are obtainable by deep etching.

TEMPERATURE COEFFICIENT OF FATIGUE

Fatigue simply means decline of observed strength with duration of loading. Its numerical value is not so easily defined, but using a temporary definition involving the ratio of the strength at a moderately short duration, divided by the strength at a long duration, both durations being arbitrarily chosen, the graph of Fig. 6 has been prepared. The errors of individual points may be considerable, but it seems reasonably clear that at low temperatures the fatigue is relatively slight. At or near the thawing point of ice, the fatigue rate jumps to a high value, remains at a high value for a couple of hundred degrees centigrade, and begins to decline as we approach low red heat.

The meaning of this seems to be that fatigue is a phenomenon of the adsorbed moisture layer.

At low temperatures, the layer is thick, but very inactive. At high temperatures it is very thin, being driven off by evaporation. In the intermediate range, where we normally experiment with glass, the layer is both thick and active, and fatigue is rapid.

Years ago J. T. Littleton said, "We never test the strength of glass: all we test is the weakness of its surface." It now appears likely that this might be amended to read, "We do not test the properties of the glass at all, but only those of the surrounding atmosphere."

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Glass-Pigment Systems

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THE physics of pigmented systems in general is very complex, and no comprehensive treatment has yet appeared. The physics of pigment systems in glass includes substantially all of the physics of ordinary pigment-vehicle systems, which do not involve a fusion process, and in addition has some other variables inherent to the use of high temperatures. These variables chiefly result from the destructive effects of molten glass on the pigment particles, which may vary from substantially nil up to such a degree of attack that the particle has ceased to exist, and is replaced by a zone in the glass, without definite boundaries, in which the composition of the glass has been changed through solution of the substance which originally was in the form of a separate pigment particle.

PIGMENTED SYSTEMS IN GENERAL

The net optical effect of pigmented-glassy layers upon the light which is incident upon them is a function of the optical properties of the particles and the matrix and the geometry of the system. The principal optical properties are the refractive index curves and the transmission or absorption curves, for the wave-lengths concerned, of the particles and the matrix. The geometry of the system involves the complete particle size distribution curve, the volume ratio, and the evenness of distribution of the particles in the matrix. These optical functions have been worked out for certain special cases of opacifier particles in paint vehicles, but an adequate general treatment for particles of high absorption or for mixtures of particles of different pigments has yet to be developed.

In consequence of these complexities, the study of pigmented systems has been approached in practice from two opposite paths. In the empirical approach, that of making glasses, for example, of given optical properties, the problem is approached purely by trial and error, without any appreciable theoretical development to accompany the experimental data. The selection of pigments, the selection of proportions, and the blending of different colored pigmented materials is carried out with respect to producing a known and a measurable optical result, but strictly on a basis of how close each trial comes to the desired result. At the opposite path of approach, we may attempt to tie together the measurable specific properties of the matrix and the particles in a completed end picture of an appearance or result produced by a relatively complicated geometric distribution. The functions can be developed part way by the use of artificially simplified systems. For example, the particles may be assumed all spherical and all of one or two given sizes. However, these are not real systems, and the transition to real systems involves so many new variables that such treatments are of limited application.

We may hope some day to be able by mathematical treatment to arrive at the net optical properties of a pigmented system by knowing or measuring merely the basic optical properties of the particles involved and the matrix material. This solution when attained will apply to all pigmented systems and not merely to glassy ones. Therefore the remainder of this discussion will be devoted to some detailed considerations of the exact nature, uses, and special properties of pigmented glassy systems, considered as a subdivision of pigmented systems in general.

PIGMENTED GLASS SYSTEMS

We must begin by saying that the word glass will be used in its broad sense, which includes not only glass as a material of construction or fabrication in itself, but also as a coating. Glasses used as coatings are the ones in which 99 percent of pigmenting is done.

The field is thus divided into two main parts, one being glass as a substance used in making containers, window panes, and useful or decorative articles generally, and the other being glassy coatings, frequently referred to as glazes or enamels. Broadly, glassy coatings are applied to

TABLE I. Typical compositions of glasses of various types.

	Fabrication glass			Claywares coatings			Metal coatings			Glass coatings	
	Boro-silicate	Window glass	Bottle glass	High temp. 1400°C	Medium temp. 1150°C	Low temp. 900°C	Sheet steel	Cast iron	Copper	Acid res.	Non-acid res.
SiO_2	80.5	71.5	74.0	71.2	50.5	38.6	50.0	24.1	30.0	31.0	14.0
Al_2O_3	2.2	1.5	0.5	13.0	10.7	6.1	6.9	6.9	—	—	—
CaO	—	13.0	5.0	6.0	5.1	5.0	—	—	—	—	—
MgO	—	—	3.5	—	—	—	—	—	—	—	—
BaO	—	—	—	—	—	—	—	7.8	—	—	—
ZnO	—	—	—	3.5	2.4	—	—	7.0	—	—	—
PbO	—	—	—	—	27.3	40.0	—	10.0	50.0	61.0	68.0
B_2O_3	12.9	—	—	—	—	8.3	10.8	10.1	—	—	12.0
Na_2O	3.8	14.0	17.0	4.3	4.0	2.0	14.0	8.6	2.5	5.0	6.0
K_2O	0.4	—	—	—	—	—	—	6.3	4.5	—	—
TiO_2	—	—	—	—	—	—	—	—	—	3.0	—
As_2O_3	—	—	—	—	—	—	—	—	5.5	—	—
Sb_2O_5	—	—	—	—	—	—	—	9.2	—	—	—
CaF_2	—	—	—	—	—	—	4.0	10.0	—	—	—
Na_3AlF_6	—	—	—	—	—	—	14.3	—	7.5	—	—

three types of bases, those made of clay or similar wares, those of metal, and those of massive glass. The glassy compositions used for each of these three main coating fields are in general distinguished by melting points. The melting points are in turn approximately limited by the temperatures which the base materials will withstand in the operation of fusing the coating on. Broadly speaking, clayware bases will stand the highest temperatures, although some types are limited in this respect, and glassy or glaze coatings on claywares therefore are applied up to temperatures of 1400°C, with special types going as low as 700°C. The next type, coatings on metals, are applied in a lower range, as metals in general will not stand the higher temperatures without detrimental effects. The highest temperatures in metal coatings are those used in applying glass to acid resisting chemical ware, in which case temperatures as high as 950°C are used. Ordinary coatings on metals are applied in the range 750°C to 850°C. In the final category, coatings on glass, the base will not stand even these latter temperatures without deformation, except for very special heat-resisting glasses. Ordinarily the glazes or enamels for use on glass must be fusible between 500 and 600°C.

Pigments in Solid Glass

The greatest part of coloring or opaquing in solid glass is done by means of solution, colloidal, or precipitation colors rather than by pigmentation in the ordinary sense. Opaque glass, and especially colored opaque glass, has in general not been desired for most uses and is not easy to make uniformly and dependably, compared to clear glass, though opal or alabaster glass is made regularly in some quantity. The coloration of glass by dissolved substances includes the use of cobalt, chromium, iron, cerium-titanium, neodymium, praseodymium, copper, uranium, and other elements. Ruby colors are produced from cadmium-selenium, gold, and copper, these systems usually being considered colloidal. White opaque glass theoretically could be made by using white opacifiers of types not rapidly soluble in the glass, such as tin or zirconium oxides, except for the fact that the relatively long melting times will dissolve a large part at least of all these substances. Practically all opaque glass is made by using fluorides, or phosphates which dissolve completely in the molten state and crystallize out during cooling, or give immiscible systems. This is a special form of pigmentation in which the pigment particles are formed in the matrix itself.

As a general statement, the reason for the scant use of preformed pigments in solid glass is simply that molten glass at its fining temperature attacks almost every known substance, and if the substance is finely divided, the attack and consequent destruction are usually complete long before the glass is ready for working. This is the result of high temperature plus fairly long time cycles. It is difficult to see much probability that

TABLE II. Typical compositions of pigments for ceramic use.

Blue	Blue-green	Green	Yellow	Red	Brown	Black	White
CoO −25	Cr_2O_3−15	Cr_2O_3−55	PbO −50	CdS −70	Cr_2O_3−25	Co_2O_3−30	SnO_2
Al_2O_3−75	CoO −10	SiO_2 −45	Sb_2O_3−35	$CdSe$ −30	Fe_2O_3−25	Cr_2O_3−35	
100	ZnO −45	100	SnO_2 −15	100	ZnO −50	Fe_2O_3−35	ZrO_2
	SiO_2 −30		100		100	100	
	100						TiO_2
CoO −40	Cr_2O_3−20	Cr_2O_3−30	SnO_2 −70	Cr_2O_3− 2	TiO_2 −75	CuO −35	
K_2O −10	CoO −40	SiO_2 −25	V_2O_5 −10	SnO_2 −50	Sb_2O_3−15	Cr_2O_3−65	
SiO_2 −50	Al_2O_3−40	CaF_2 −25	PbO −20	SiO_2 −20	Na_2O− 8	100	
100	100	CaO −20	100	CaO −28	Cr_2O_3− 2		
		100		100	100		

this situation will change radically, except possibly by trying to introduce pigments at a late stage in the glass making operation, so that they will be less subject to attack.

When pigments are destroyed, their disappearance may in different cases be due to pure thermal change, to oxidation, volatization, metathesis, or to solution.

Pigments in Glassy Coatings

The subject of special glass compositions and their pigmenting for coating applications is one of great variety. They are nearly all silicates and may furthermore be broadly divided into alkali or alkaline-earth silicates, and lead silicates. Generally speaking, the alkali silicates are used for higher temperatures and the lead silicates for lower temperatures. This classification is loose and has exceptions. Another broad generalization is that in general the higher the melting point, the greater the chemical inertness, and this principle is a basic guiding one for many applications.

Merely as illustrative, and to show the type of compositions involved, we tabulate herewith (Table I) typical melted weight percent compositions of some glasses used in solid form for fabrication and some used as coatings.

These compositions have been selected from the large number available in published references, on the basis of representing an average usage for the types of work tabulated. The selections were made from Morey, *The Properties of Glass;* Andrews, *Enamels; Ceramic Industry* (January 1942); and U. S. Patent 2,251,161.

It will be seen on inspection of this table what a wide composition range occurs in glass usages. A very large amount of broad study on glassy systems has been carried out, especially at the Geophysical Laboratory, but the number of variations is so great that much remains to be done. Unfortunately, many of the glassy systems are found empirically to be at the best combination of properties with more than three components, in fact even as many as eight. This fact militates seriously against the possibility of extensive systematic studies, due to the enormous number of permutations involved.

Glasses used as coatings are formulated with respect to many properties including softening temperature, viscosity coefficient, coefficient of thermal expansion, chemical reactivity or lack of it, proneness to devitrify or crystallize, and often other special requirements. Sometimes the question of absence of reactivity with certain important pigments becomes dominating, as certain compositions, satisfactory otherwise, must be ruled out on this account. Every change in the composition of a glass which makes a measurable change in one property usually changes the others as well. This precludes any simple straightforward way of arriving at a glass composition for a particular purpose, and when extreme refinement in some special property is needed, the search becomes empirical in great degree.

Practically all of these glasses used as coatings are pigmented. The pigmented glassy coatings are not in basic principle different from paints. They may with perfect justice be pictured as paints which assume their fluid condition only at high temperatures, whereas ordinary paints are fluid at room temperature and become hard by loss of solid from the paint layer and setting

reactions in the vehicle rather than by simple increase in viscosity on cooling. All the usual considerations which must be kept in mind for optical analysis of any paint system also apply here. These include the thickness of the layer, the exact kind and amount of pigmentation, and the characteristics of the base or background material. In addition, as mentioned previously, many of the pigments used in glassy systems react to a greater or less extent with the matrix. Furthermore, this extent of reaction is not by any means a uniform characteristic of a given pigment, but even for one pigment may cover a wide range of variation depending upon the composition of the glass and the temperature and time in contact. Generally speaking, the lower the temperature the less reactivity, even though the fluidity of the glass may be greater at the lower temperature.

PIGMENTS USABLE IN GLASSES

The pigment systems used in coloring glasses are in general not the same as those used for paint pigments. This is primarily because of the necessity for withstanding both the heat and the attack of the molten glass, which limitations bar out nearly all paint pigment types. On the other hand, very few ceramic pigment types are usable in paints because in developing the necessary stability, so much is sacrificed in the way of optical pigment properties as to render them practically unusable in competition with regular low temperature types of greater intensity.

Again as illustrative, we tabulate herewith in Table II typical compositions for some of the main high temperature pigment types used for work in glassy systems.

The illustrative compositions shown here are those calculated from the batches used. As in most pigment work, the tinctorial properties of the finished pigment material under conditions approximating those of use are the guiding consideration, and recourse is had to analysis only in special cases.

The oxides shown may be combined in various ways. In some cases, careful studies have established the existence of definite and quite stable compounds, and in other cases there is apparently the formation of solid solutions. Since most of the empirical compositions do not have the exact ratios of compounds, there probably is present most of the time an excess of one component, so that the net picture of the pigment probably is that of a mixture of several types of colored compounds intimately admixed.

The pigments are formed either by reactions between co-precipitated hydroxides or carbonates, or more usually by thermal reactions between the oxides themselves, usually carried out between 1000° and 1400°C for periods of one to eight hours. The velocity of reaction generally becomes much less below 900°C, and except for cadmium sulphoselenides and copper-chrome blacks, the lower temperatures are less used.

SUMMARY

The highlights of the subject of pigmented glasses may be summarized very briefly:

(1) Pigmenting of ordinary glass is infrequent because the pigments will not remain as such during long meltings.

(2) Pigmenting of glasses used as coatings is of great commercial importance.

(3) There is no intrinsic difference from the viewpoint of physical optics between a pigmented glass layer and a pigmented paint vehicle layer, and the broad treatment for one will do for the other.

(4) There tends to be some pigment destruction even in glasses used as coatings, and to the extent to which this occurs, it greatly complicates any mathematical development.

(5) The enormous diversity both of glass types and high temperature pigment types makes it necessary to study any given system or combination at considerable length in order to formulate its optical behavior in any significant way.

The Darkening of Materials by Light

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1. INTRODUCTION

BOTH crystals and glasses are composed of atoms. As Professor Warren has shown, the principal difference between the two materials lies in the difference in the arrangement of the atoms they contain. In crystals, this arrangement is highly regular, being patterned after a three-dimensional lattice, whereas in glasses only the relative arrangement of neighboring atoms is repeated with any degree of regularity from one part of a given specimen to another. As a result of this identity of the building units in glasses and crystals, we should expect these materials to possess many properties in common, namely, any property whose source lies in the constitution of the atoms that are present rather than the atomic arrangement. The phenomenon of photolysis, or darkening by light falls in this category. This property is widely observed in many crystalline pigment materials and in many glasses. In certain cases, such as that of silver bromide, it is very useful and has been studied in order that it may be enhanced; however, it is more commonly a detriment and in these cases the purpose of research is to find a method of eliminating or controlling it.

The purpose of this brief paper is to summarize from an atomic standpoint the basic principles that govern photolysis.

2. THE INTERACTION BETWEEN ATOMS AND LIGHT

Atoms are composed of a central positively charged nucleus about which negatively charged electrons are swarming. Under the conditions in which photo-darkening ordinarily occurs the electrons and not the nuclei react with the radiation. However, the extent to which they react depends greatly upon the manner in which they are bound to the nuclei. For example, the electrons in singly charged ions, such as those found in sodium chloride or in a soda-lime glass are so tightly bound that they intereact with, or absorb, only wave-lengths far beyond the visible or ultraviolet regions of the spectrum of ordinary interest. On the other hand the electrons on neutral atoms that have been trapped within solids, or on transition-metal ions such as chromium, are much more reactive. This reactiveness is made evident, of course, by the fact that they absorb radiation in the wave-length range of interest. In fact we may expect a material to be sensitive to light in a given range whenever it absorbs in this range. When we are concerned with sunlight, this is true, for example, of colored glasses and pigments and of those materials, such as zinc sulfide or titanium dioxide, which, though white, absorb in the near ultraviolet. Similarly, we may anticipate some degree of light sensitiveness in materials which absorb in the air-transmitting range of the farther ultraviolet between 1850A and 3000A if they are exposed to the radiation of a mercury arc since this is rich in wave-lengths in this range.

Although a material can be sensitive to light only if the electrons of one of its constituents are sensitive to light, it does not automatically follow that it will darken if exposed to light in the absorbing region. It appears to be necessary, as the examples which will be discussed below show, that certain secondary changes in the material occur just after the electrons have absorbed radiation. If these changes do not occur, the absorbed energy may be dissipated either as light or as heat without altering the material. On the other hand, when these secondary changes do occur, part of the absorbed energy may be stored in the form of an electronic rearrangement which is capable of absorbing new wave-lengths in the visible part of the spectrum and hence of discoloring the material. We shall now consider in detail the manner in which this change comes about in several cases that have been studied in detail.

3. THE COLORED ALKALI HALIDE CRYSTALS[1]

Pure alkali halide crystals ordinarily are colorless and transparent. Moreover, they do not have appreciable absorption in the air-transmitting region of the ultraviolet spectrum. If, however, the crystals are heated in the presence of alkali metal vapor, they become discolored. The nature of the new absorption depends upon the particular alkali halide with which we are dealing, but can invariably be represented by a bell-shaped absorption peak of the type shown in Fig. 1. Careful chemical analysis has shown

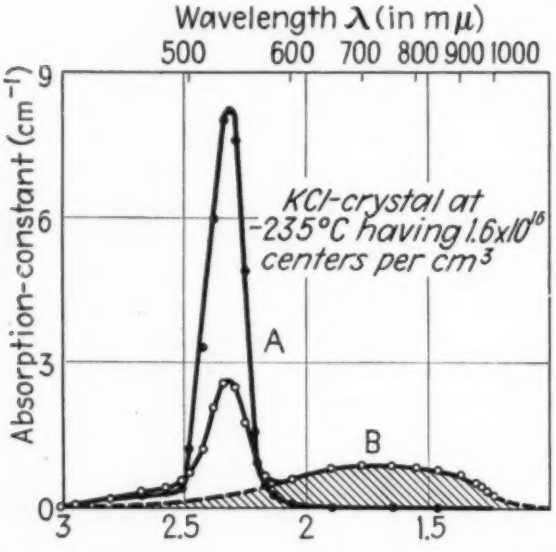

FIG. 1. Curve *A* represents the absorption of the color centers in a colored potassium chloride crystal as a function of wave-length. Curve *B* represents the absorption after the crystal has been irradiated for a period of time with light lying in the original absorption band. It may be seen that the original peak has been decreased and that a new peak, which lies farther toward the red end of the spectrum has been produced.

that the crystals heated in the presence of the alkali vapor contain an excess of alkali metal atoms. These atoms diffuse into the crystal as ions; however, the associated valence electron also diffuses, so that the crystal remains electrostatically neutral. These electrons do not return to the alkali metal ions when both are inside the crystal, but instead occupy positions left by halogen ions that have diffused to the surface of the crystal. When in these positions the electrons are able to absorb light in the visible region of the spectrum. As a result of their discoloring influence, these electrons are called *color centers*.

Let us now suppose that the crystal containing color centers is irradiated with light in the absorption band. It turns out that during such irradiation, the original absorption band fades and is replaced by the second absorption band shown in Fig. 1. This evidently is a very elementary type of photolysis in which irradiation causes a shift in color. The experimental evidence dealing with the process shows that during irradiation the electrons that absorb light receive sufficient energy to become free to roam about in the lattice. Some of them return to vacant halogen sites of the type they have left, but others become trapped at vacant sites already occupied by electrons. Since they are not as tightly bound to the second type of site because of the repulsive action of the electron already there, they may absorb radiation of lower energy, or longer wavelength. Hence their absorption peak is shifted to the red. The electrons in the new type of center will return to the old type if the crystal is heated sufficiently. During this heating they become free again and wander about until they find an unoccupied halogen vacancy of the type to which they were originally bound. Thus the change in color produced by irradiation is reversed by heating after irradiation.

The migration of the electrons during the original irradiation can be detected by imposing an electric field on the crystal and observing the flow of current that accompanies the motion imposed on the electrons by the field. The experimental set-up used in such measurements is shown schematically in Fig. 2. The electric field is produced by the set of batteries shown in the circuit and the current is measured by a comparatively sensitive galvanometer or electrometer. In the case of the colored alkali halides, the photo-current is observed at the instant the irradiation begins and, at room temperature, ceases as soon as the light is extinguished. When the crystal is warmed the current continues for a short period after irradiation because the trapped electrons wander about until they find the vacant sites of the type occupied originally.

In this example, it is essential for the production of the shift in color that the electrons become free after they have been excited by absorption of the incident light during the irradiation. If they did not, they would presumably fall back

to their original state with the emission of light or heat and the system would be unaltered. There is evidence to show that the electrons are not freed by the action of light alone and that heat is necessary for completion of the process. That is, the action of light raises the electrons to discrete levels in which they are still bound to the nuclei and the additional excitation for freeing is furnished from the thermal motion of the lattice. The evidence for this is given by the fact that the photo-currents described in the preceding paragraph are not observed when the colored salts are cooled to very low temperatures, even though they continue to absorb radiation. The change in color also is not observed at these temperatures. As remarked in the introduction, there frequently is an intermediate step in the darkening process, such as that represented by the thermal freeing of electrons in the present example.

4. THE DARKENING OF SILVER BROMIDE[2]

Silver bromide decomposes under the action of light lying in the blue and near ultraviolet spectrum of the crystal. Careful chemical work has shown that the products of decomposition are free silver and bromine. In this process, as in the preceding one, the crystals become photoconducting under the action of the light that induces the decomposition. Thus it follows that electrons are freed under the action of light and wander about in the lattice. There is, however, a striking difference between this case and the previous one. It is found that the decomposition can be prevented by cooling the material to liquid-air temperatures; however, the photoconductivity does not disappear at the same time. This shows that the critical secondary stage in the process is not the thermal freeing of excited electrons, as in the preceding case.

When the silver bromide is irradiated in bulk form the free silver and bromine remain sufficiently close together so that they can reunite if the specimen is heated and diffusion is promoted. However, the bromine diffuses away when the bromide is finely dispersed and is emersed in gelatine, as in an actual photographic emulsion, so that the process is less reversible in this case.

The explanation of the darkening process that

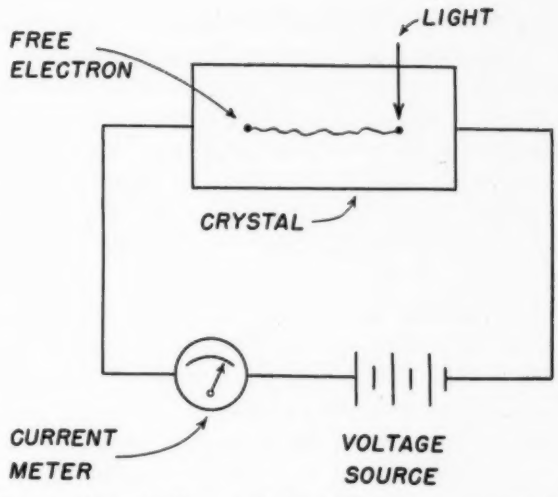

FIG. 2. Schematic diagram of the circuit used to measure the conductivity induced in a crystal during irradiation.

appears to correlate all of the known facts was developed as the result of the contribution of many investigators; however, the credit for the final form is due to Mott and Gurney. This theory is as follows: The photoelectrons that are detected during irradiation are ejected from bromine ions and wander about the lattice until they become trapped. The nature of the trapping centers in bulk crystals of silver bromide is not certain; however, there is good evidence that they are small specks of silver sulfide in the granules of a photographic emulsion. These specks have strong affinity for the electrons and apparently can hold them indefinitely once they have trapped them. As a result of the presence of these electrons, the trapping centers become negatively charged. If a compensating positive charge did not flow to them in order to neutralize this negative charge, they would eventually repel additional electrons. If this were to occur the free electrons would have no alternative other than to wander about until they find the atoms from which they were freed originally and light would have no further effect on the crystal. It so happens, however, that silver bromide is a feeble ionic conductor at room temperature. Part of this conductivity is due to mobility of the positively charged ions of the lattice. As a result, silver ions migrate to the charged centers and neutralize them. In so doing the ions become transformed to neutral silver atoms. Thus it may be said that in this case the action of the light is

to produce electric fields which succeed in electrolyzing the silver bromide because of its inherent ionic conductivity. The same end result, namely, the production of free silver and bromine, evidently could be achieved by placing electrodes across a specimen and charging them sufficiently to cause an ionic current to flow and to deposit the constituent elements at the electrodes. The "photoelectrolysis" stops at liquid-air temperatures because the ionic conductivity is not sufficiently great. Thus the results of the flow of ionic current represent an essential intermediate stage in the photolysis. It might be supposed that, as in the example discussed in the preceding section, the photolysis would also be stopped at low temperatures because thermal energy is needed to free excited electrons from the chlorine ions. This evidently would make itself apparent as a decrease in photo-conductivity of the type observed in the colored alkali halides. However, experiments have not yet been carried out at sufficiently low temperatures to produce the effect.

5. THE DARKENING OF ZINC SULFIDE

Ordinary zinc sulfide of pigment type will darken when exposed to radiation lying below 3200A. Chemical analysis shows that in this case the darkening products are free zinc and sulfur; moreover, it is found that the type of zinc sulfide that darkens is a good photo-conductor. These facts suggest on the surface that there is a close analogy between zinc sulfide and silver bromide. Closer inspection reveals, however, the following striking differences between the two cases:

(a) Zinc sulfide is not naturally photo-conducting, but becomes so only after it has been calcined. The material which has not been calcined does not darken.

(b) The sulfide will not darken if it is thoroughly dry.

(c) Photo-conductivity is induced in zinc sulfide by wave-lengths longer than those which produce darkening as well as by the darkening radiation.

(d) Zinc sulfide is not an ionic conductor.

The theory of darkening that correlates all of these facts is as follows. Although uncalcined zinc sulfide absorbs radiation below 3150A, the electrons that become excited are not made free, so that there is no direct change produced in the material. During calcination, the sulfide decomposes partially, sulfur atoms evaporating from the surface and leaving behind a stoichiometric excess of neutral zinc atoms. These atoms diffuse into the crystal in much the same manner as the sodium atoms in the colored alkali halides; however, the interstitial zinc atoms probably retain their electrons in this case. The valence electrons are comparatively loosely bound to the neutral zinc atoms and may be freed at room temperature by near ultraviolet radiation lying as far toward the visible as 3600A. The freed electrons wander about in the lattice and may become trapped like the electrons in silver bromide. However, since the material is not an ionic conductor, the trapping centers receive no neutralizing positive charge when the exciting wave-length is longer than 3200A and the process is blocked—as would occur in silver bromide if there were no ionic conductivity.

Now when the photoelectrons are ejected from the neutral zinc atoms they leave behind a positively charged zinc ion. It may be shown that this ion can be neutralized by an electron from a nearby oxygen ion if light waves of sufficient energy are supplied to the oxygen atoms. Moreover, it can be shown that the positive charge which is thereby transferred to the oxygen ion is mobile in the sense that it can migrate from one ion to another. It appears that radiation lying below 3200A is effective in neutralizing the zinc ions that are formed when the photoelectrons are ejected and in producing the mobile positive charges. Thus although radiation as long as 3600A is sufficient to produce photoelectrons, the shorter radiation is required to insure that mobile charges of both signs are generated. It is reasonable to assume that the carriers of both signs migrate until they either meet and neutralize one another or until they become trapped. In the first case the result is merely the evolution of light or heat, whereas in the second electrostatic fields are produced which could result in electrolysis if ionic conductivity were possible. This conductivity can be furnished by a surface film of moisture in which both zinc and sulfur ions are probably slightly mobile. Thus the photolysis can proceed if this film of moisture is

present, but is prevented otherwise because of the absence of internal ionic mobility.

To summarize, the photolysis of zinc sulfide can be explained by assuming that the light generates electric fields which serve to electrolyze surface ions that are made mobile as the result of a surface film of moisture. It is well known that the darkening can be inhibited by the addition of small traces of cobalt to the sulfide. Although the influence of cobalt has not been studied in detail, it seems likely that it either interferes with the production of free electrons or serves to trap them and the migrating positive charges produced by the short radiation.

6. THE DARKENING OF LEAD CHROMATE

During the past three years the experimental group at the University of Pennsylvania under the direction of Professors Lawson and Miller has been engaged in a study of the darkening of lead chromate. This work has been given very essential support by the Newark group of the Krebs Pigment Division of E. I. du Pont de Nemours and Company. It has been shown that the factors influencing the darkening of lead chromate are somewhat more complex than in the preceding cases and, in fact, combine many of the features of all of them. This work will be published in a series of papers during the coming year.

7. OTHER TYPES OF DARKENING BY LIGHT

In all of the foregoing examples the darkening is accompanied by photo-conductivity. Although the two phenomena are undoubtedly closely connected in many cases, there are also cases in which darkening is not accompanied by photo-currents. The writer recalls crystals of commercial magnesium oxide that turned a deep violet under irradiation by the light from a mercury arc and yet showed no evidence of photo-conductivity. The same is probably true of many common glasses which are discolored by ultra-violet light. In all such cases with which the writer is familiar the effects of darkening can be completely reversed by application of heat.

Although examples of this type have not yet been investigated with the same degree of thoroughness as the preceding cases, it can undoubtedly be said with confidence that in each instance electrons are excited but not freed by absorption of light. However, while the electrons are in the excited state, molecular rearrangements occur in the vicinity of the excited electrons which serve to trap the electrons in metastable excited states. When in these states, the electrons are able to absorb wave-lengths in the visible portion of the spectrum and hence discolor the material. The application of heat reverses the molecular rearrangement and allows the electrons to return to their original state. Investigation would undoubtedly show that in many cases the original molecular rearrangement is also thermally induced, so that darkening is inhibited at sufficiently low temperature.

8. CONCLUSION

We see then that most of the cases in which darkening by light has been studied, the process falls into a fixed pattern. Certain of the electrons contained in the material are excited by absorption of radiation. These may be either electrons of the bulk material or electrons on certain specific impurity atoms or lattice defects. When the electrons are in the excited state, secondary processes occur which allow the electrons to remain in an excited state and absorb wave-lengths which are different from those they absorbed originally. The darkening process frequently can be reversed by application of heat since this allows the excited electrons to return to their original state.

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2. A summary of the work on silver bromide is given in the book by Mott and Gurney quoted in reference 1.
3. See the paper by N. T. Gordon, F. Seitz, and F. Quinlan, J. Chem. Phys. **7**, 4 (1938).

New Books

The Electron Microscope

By E. F. Burton and W. H. Kohl. Pp. 283, Figs. 134, 16×23½ cm. Reinhold Publishing Corporation, New York, 1942. Price $3.85.

This book has apparently been brought out with the laudable purpose of acquainting the lay public with the physical principles underlying the operation of the electron microscope. To this end it contains very elementary discussions of wave motion, light, electrostatics, electromagnetics, and electron optics, which occupy the first two-thirds of the text. The style is chosen with a view to interesting readers without scientific background beyond high school physics and the illustrative diagrams are accordingly vivid and (where possible) amusing. It is unfortunate, therefore, that several of the statements are confusing, or, in a few cases, inaccurate. For instance, on page 65, "we have the curious phenomenon of light from two sources, *A* and *B*, traveling independently to a screen and, with no obstacle involved, producing darkness at some points on the screen." Curious indeed! Taken alone, this statement corresponds to no known experiment and, even in its context, is misleading. Again, Fig. 85a on page 153 illustrates the formation of a real image by a diverging lens. That such a lens has "no practical value" (page 155) seems an understatement. Also, in the discussion of magnetic focusing, no explanation of the action of a short magnetic lens is given, although the background for such an explanation is quite fully covered. This reviewer feels, therefore, that the public to which the text is directed runs danger of being confused and misled by it, while the more technical public has little to learn therefrom.

On the other side of the ledger stands the extremely interesting set of reproductions of electron micrographs with which the text is interleaved and which are in themselves a sufficient excuse to own this volume.

David Harker
General Electric Company

Electromechanical Transducers and Wave Filters

By Warren P. Mason. Pp. 333+xii, Figs. 120, 16×23½ cm. D. Van Nostrand Company, Inc., New York, 1942. Price $5.00.

This book sets forth the fundamental analogies between electric circuit theory and mechanical theory and shows the solution of mechanical, acoustical, and electromechanical vibrating systems in terms of their equivalent electrical circuits. The first half of the book reviews electric circuit theory, including filter structures, with both lumped and distributed constants. These electrical network equations are then applied to the solution of vibrating mechanical systems having lumped constants as well as to the solution of problems dealing with acoustic wave propagation including sound transmission through conduits and acoustic filters. In the second half of the book, electromechanical transducers receive particular attention. Of special interest is the problem of the piezoelectric transducer which is solved in terms of its equivalent electrical circuit in which the numerical values are given for quartz and Rochelle salt. In order to produce high efficiency transducers, the mechanical system is treated as a portion of an electromechanical band pass filter and the remainder of the filter circuit is made up of electrical elements to give negligible loss over a relatively large portion of an octave. Another subject that is very well treated is that of electromechanical wave filters in which low loss vibrating mechanical elements, such as quartz, form part of the filter circuit thereby resulting in very sharp frequency selectivity. The subject matter is quite mathematical in nature and the book will appeal particularly to those having a good background of electric circuit theory and mathematics.

Frank Massa
The Brush Development Company

Applied Mechanics and Related Subjects, Theodore von Kármán Anniversary Volume

By the Friends of Theodore von Kármán. Pp. 337+xv, Figs. 78, 22½×28½ cm. California Institute of Technology, Pasadena, 1941. Price $3.75.

This book is a collection of scientific papers presented by a small number of Professor von Kármán's close friends who are outstanding workers in the field of applied mechanics. As stated in the preface, the volume is meant to express the sincere congratulations of these friends on the occasion of his sixtieth birthday.

The book begins with an appreciation of Professor von Kármán by Clark B. Millikan. Then follows the very impressive list of von Kármán's published works, consisting of ninety-one papers on applied mechanics, physics, hydrodynamics, and aerodynamics as well as general engineering subjects. Next follow twenty-six papers each written by a distinguished colleague of Professor von Kármán. It is impossible in a review of this kind to analyze the papers individually. However, as a guide to those interested in the book, the subjects covered are the following:

Some definite integrals occurring in aerodynamics by H. Bateman;
On the geometry of streamlining by Max M. Munk;
Dimensional analysis and similitude in mechanics by J. C. Hunsaker;
Impulse and momentum in an infinite fluid by Theodore Theodorsen;
Coriolis and the energy principle in hydraulics by Boris A. Bakhmeteff;
The influence of bottom topography on ocean currents by H. U. Sverdrup;
Ionization as a factor in fluid mechanics by W. F. Durand;
Isotropic turbulence in theory and experiment by Hugh L. Dryden;
The intrinsic theory of elastic shells and plates by J. L. Synge and W. Z. Chien;
The compressibility of solids under extreme pressures by Francis D. Murnaghan;
Hydrodynamics and the structure of stellar systems by F. Zwicky;
On the elastic distortion of a cylindrical hole by a localized hydrostatic pressure by H. M. Westergaard;
On the absorption of sound waves in suspensions and emulsions by Paul S. Epstein;
On a method for the solution of boundary-value problems by R. Courant;
The engineering treatment of ring or wheel problems by Karl Arnstein;
On the five-dimensional representation of gravitation and electricity by A. Einstein, V. Bargmann, and P. G. Bergmann;

The forced vibrations of tie-rods by S. Timoshenko;

A note on the effect of the wind-tunnel size on pitching moments by Th. Troller;

The creep of metals under various stress conditions by A. Nádai;

On the minimum buckling load for spherical shells by K. O. Friedrichs;

The theory of flow through centrifugal pumps by William Bollay;

The ideal performance of curved-lattice fans by Frank L. Wattendorf;

Stress concentrations due to elliptical discontinuities in plates under edge forces by L. H. Donnell;

On lubrication flow with periodic distribution between prescribed boundaries by Hans Reissner;

Some remarks on the laws of turbulent motion in tubes by R. v. Mises;

Stress pattern crazing by Wolfgang B. Klemperer.

The text for this anniversary volume has been well printed by the offset process and the book is durably bound. It seems certain that all friends of von Kármán will want a copy of this volume.

E. HUTCHISSON
National Defense Research Committee

Reports on Progress in Physics, Volume VIII

W. B. MANN, general editor. Pp. 372+ii, Figs. 57, 18½×25½ cm. The Physical Society, London, 1942. Price $5.25.

The physicists of Great Britain are to be complimented on the production of a volume of this kind at the present time. It has not been done without much labor, nor without help. The Editor, remarking that "the task of soliciting *Reports* in war-time is comparable with that of the biblical maker of bricks after a lean wheat year," acknowledges the assistance of several colleagues on both sides of the Atlantic. Of the fourteen separate papers, about half are by British, the remainder by American authors.

As data accumulate, more and more it becomes impossible even for those whose life work is in physics to be familiar with the latest subtle details in any but a small portion of the whole field. The time has long passed since a Thomas Young could enjoy the reputation of knowing all that was worth knowing about science. Here is a volume which will provide every physicist with readable and interesting information without burdening him with controversial details which, in time, will gradually settle down into their rightful perspective.

With a few exceptions, which depend on the bent of the reader, the Reports are presented at a very consistent level, and in a pattern which endeavors to throw each subject into its just position in the development of physics. They are not compressed summaries of a few of the most recent papers, but reviews of different topics over a period of ten or twenty years up to the middle of 1941. Should a young man yearn to tackle a research problem related to the subject matter of one of these Reports, he could find no better introduction to his reading than the material provided here. If the bibliographies be included, the amount of information is large indeed.

The introductory article, by Professor Born, on "The teaching of theoretical physics in universities," reflects the current interest in the training of young physicists who are now so urgently in demand. It is, of course, true that different curricula are probably required to meet the specific needs of different countries, but it is important to remember that the content and integration of the curricula should not be subordinated to methods of organizing them. Our American colleges are not entirely blameless in this respect. A flexible curriculum, which permits a student to transfer at almost any moment from one college to another without interrupting his studies, has led American colleges to partition the subject matter of physics into compartments repsented by advanced undergraduate courses in Mechanics, Electricity, Optics, Heat, X-Rays, and the like, to such an extent that, in American teaching, either the illuminating cross-relations between the various topics must be lost to view, or else the courses must involve an unreasonable overlapping of subject matter. Between this extreme, and the British one of twenty years ago when the subject matter of advanced courses was frequently a matter of the whim or interest of the professor, there must surely be a useful compromise. To hit the house between wind and water a cooperative post-war effort will be needed.

We have picked out Professor Born's article for special comment merely because it is unique in that it deals with methods, while the remaining papers deal with the subject matter of physics. Most of these deserve reviews in their own right. The list of items given below could be multiplied fifty-fold without exhausting the volume of factual material.

A fairly uniform sampling reveals information on topics like these: the limitations of the Debye theory of specific heats; the faults of the hardest steels and the merits of others in the manufacture of centrifuge rotors; the part which formaldehyde plays in the knocking of internal combustion engines; the mechanism of sliding friction from the viewpoint of relaxation oscillations; the importance of applying (or of failing to apply) group velocity corrections in determinations of the velocity of light; the antiquity of the fundamental discoveries on which modern television practice is based; modern Schmidt cameras, and late news of the corona; the operation of the M.I.T. automatic wave-length comparator and interval sorter; the meaning of a standard candle, or what it would have meant had war not again marred the earth; and the mechanism of the spark discharge—a word picture in slow motion. A few of the Reports will appeal more to the specialist than to the general reader, particularly those dealing with molecular spectra, with symmetry properties of nuclear levels, and with special properties of crystals and liquids in the far infra-red.

The abrupt but topically illuminating change in the color and quality of paper before the end of the book brings to mind a tale, perhaps apocryphal, of Allenby's Palestine campaign twenty-five years ago, when, owing to the scarcity of supplies, dispatches were reported to have been written on paper designed for quite another purpose. In the present case, however, notwithstanding the Editor's conscientious apology, neither the usefulness nor the appearance of the publication is significantly impaired.

Do not put this volume in your book case; put it on your desk.

THOMAS H. OSGOOD
Michigan State College

Here and There

Recent Appointments

Dr. Paul Herget, Assistant Professor of Astronomy at the University of Cincinnati, has been granted leave of absence for the duration to accept a war appointment to the Nautical Almanac Office of the U. S. Naval Observatory, Washington, D. C.

The Roller-Smith Company, Bethlehem, Pennsylvania, announces the appointment as Assistant Chief Engineer of Roy M. Smith, who has previously been associated with the Bryant Electric Company and the Westinghouse Electric and Manufacturing Company.

Dr. Frederick W. Sullivan, Jr., Director of Chemical Research of the Barrett Division of Allied Chemical and Dye Corporation, has been appointed Technical Director of the Institute of Gas Technology. The Gas Institute was founded in 1941 and is affiliated with the Illinois Institute of Technology. It is the only institution in the country where students may work for graduate degrees in gas technology.

F. C. Todd, of the Pennsylvania State College, has joined the technical staff of Battelle Memorial Institute, Columbus, Ohio, where he will undertake research in industrial physics.

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Annual Fall Meetings

The 27th annual meeting of the Optical Society of America will be held at the Hotel Pennsylvania in New York City on October 30 and 31. The program for Friday, October 30, includes a symposium in the morning on "Optical Instruments," a second symposium in the afternoon on "Mathematics in the Field of Optics," as well as the annual dinner which will take place Friday evening.

The American Mathematical Society and the Society of Rheology will also meet at the Hotel Pennsylvania at the same time. A joint luncheon of the three societies is planned for October 30.

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New and Rare Instruments

Urgent requests from research workers have been received by the Committee on Location of New and Rare Instruments for the following:

Microammeters and electrical meters generally.
Ultraviolet microscope.
Zeiss optimeter (for measuring fine wires to 0.00001 inch).
Two-circle reflecting goniometer (Goldschmidt).
Electro-encephalograph (3 channel).
Warburg apparatus.

If you have any of these instruments available to lend, lease, or sell, please write to Dr. H. Killefer, Chairman, 60 East 42 Street, New York, New York.

The following instruments are offered for use, and inquiries concerning them are invited:

Zeiss-Pulfrich refractometer.
Hunter reflectometer (Infra-red reflectance).
Capacigraph (J. Lab. and Clinical Med. **22**, 1279 (1937); **25**, 175 (1939)).
Coleman spectrophotometer (complete).
Mechanical ink writing recorder (Am. J. Obstet. and Gynecol. **40**, 330 (1940)).
Grating spectrograph: Focal length 2 meters
Dispersion 8A/mm, first order.
Grating spectrograph: Focal length 8 meters
Dispersion $\frac{1}{4}$A/mm, fourth order.

The Committee on Location of New and Rare Instruments of the Division of Chemistry and Chemical Technology, National Research Council, will be glad to put inquirers into appropriate contact with those who can supply their needs. In so doing, the committee assumes no responsibility, and owners of instruments must make their own arrangements with prospective users. All correspondence should be addressed to Dr. Killefer.

★

Scientific Shorts

The L. B. Fischer Publishing Corporation announces a proposed series of low priced ($1.25) pocket-size books dealing authoritatively with various aspects of modern scientific knowledge, to be issued under the general title *Treasury of Science*. The Board of Editors includes Professor Harlow Shapley of Harvard University, Dr. Alvin Johnson, Director of the New School for Social Research, and Dr. Alfred E. Cohn of the Rockefeller Institute.

It is hoped that this series will fill the need for substantial and standard scientific literature, presented expertly but not pedantically, and available at a moderate price. Each book will consist of some 200 pages of clear readable type with adequate illustrations on easily handled paper. The books will be of uniform size, $4\frac{1}{4}$ by $6\frac{3}{4}$ inches.

It is the publishers' intention to add at least 24 volumes every year until the *Treasury of Science* represents a complete library of our present scientific knowledge. Correspondence on manuscripts is invited. Please write to *Treasury of Science*, L. B. FISCHER PUBLISHING CORPORATION, *381 Fourth Avenue, New York, New York.*

★

New Series on Radio Communication

The McGraw-Hill Book Company announces a new series of technical books in the field of radio communication engineering, under the consulting editorship of Beverly Dudley, acting Managing Editor of *Electronics*. This series is designed to provide an integrated and well-coordinated program of texts which will cover the various specialized branches of communication which have been developed in the last two decades.

As originally outlined, the series calls for texts on: Basic mathematics for communication engineers; Principles of electricity; Introduction to radio engineering; Fundamentals of electric circuits; Electrical filters; Transmission lines and wave guides; Antennas and radiation phenomena; Electron tubes in communication; Frequency modulation; Ultra-high frequency technique; Acoustics and electromechanical devices; Communication measurements.

Correspondence is solicited with prospective authors and users by both the consulting editor and the publishers for suggestions as to authors or additional volumes which might be included in the series.

Contributed Original Research

Rate of Crystal Growth in Drawn Tungsten Wires as a Function of Temperature*

C. S. Robinson, Jr.
Massachusetts Institute of Technology, Cambridge, Massachusetts
(Received July 1, 1942)

Large single crystals can be grown in "218" and similar tungsten wires by vacuum heating at a constant temperature in the range 1900°K to 2200°K. The growth can be followed by observation of the thermionic emission pattern, using a cylindrical electron-projection tube with a fluorescent screen. The rate of growth is found to increase with temperature according to an exponential law. Crystal growth is slower in wires drawn to smaller diameter; this can be explained by the *small grain hypothesis*. The perfection of crystals is discussed.

I. INTRODUCTION

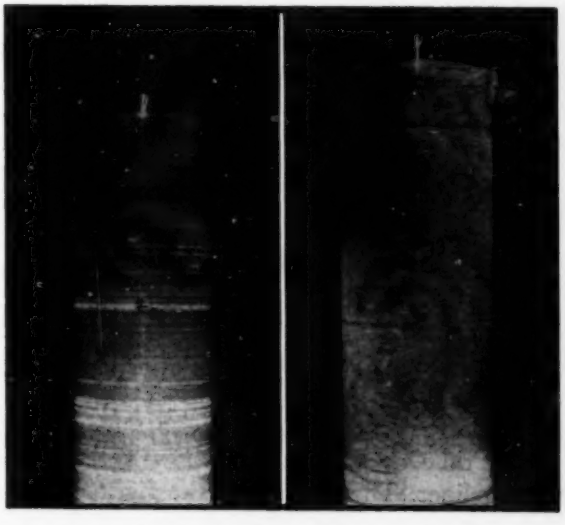
Nelson[1] produced single crystals several centimeters long in "218" tungsten wire by raising the temperature slowly from 1000°K to 2600°K. The author has shown that large crystals can be grown by heating in vacuum at a constant temperature. The growth can be followed by observation of the thermionic emission pattern, using a cylindrical electron-projection tube with a fluorescent screen.[2,3]

II. EXPERIMENTAL PROCEDURE

Two kinds of tungsten wire were extensively studied: G. E. Lot No. 218 "non-sag" wire, and G. E. Lot No. 361 WAHF "super-non-sag" wire. These wires will be referred to as 218 and 361.

The initial diameter of the wires used was 3 and 5 mils. Each wire was ground[4] until only a few small scratches were visible under a high power microscope. In most cases comparisons were made between wires ground just enough to remove the die-marks (about 0.2-mil reduction in diameter is sufficient) and wires ground to 60 percent of their initial diameter.

If the grinding was carefully done, the wires contained 25-cm lengths of uniform diameter, the total variation usually being less than 0.1 mil. These lengths were mounted with a suitable spring along the axes of cylindrical projection tubes, which were evacuated and usually gettered and sealed off with a pressure of 10^{-7} mm Hg or lower. The temperature of the wire was determined from the current function of Jones and Langmuir.[5]



(a) (b)

Fig. 1(a) 2 min. at 2100°K. (b) 52 min. at 2100°K.

* Submitted to the Graduate School of the Massachusetts Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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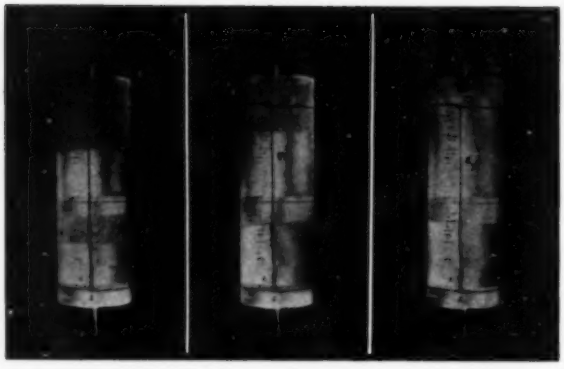
[3] M. H. Nichols, Phys. Rev. **57**, 297 (1940).

[4] R. P. Johnson, A. B. White, and R. B. Nelson, Rev. Sci. Inst. **9**, 253 (1938).

[5] H. A. Jones and Irving Langmuir, Gen. Elec. Rev. **30**, 310 (1927).



(c) (d) (e)

FIG. 1(c) 1.52 hr. at 2100°K. (d) 1.87 hr. at 2100°K. (e) 17 hr. at 2100°K.

III. RATE OF GROWTH *VS.* TEMPERATURE

Experiment soon showed that one-half hour of heating at 1800°K during evacuation did not affect subsequent crystal growth; a wire so treated will be referred to as a raw wire.

If at time $t=0$ a raw wire is brought rapidly to some temperature T above 1900°K, and an accelerating voltage (4000–10,000 v) applied to the collector, a number of bright rings appear on the screen. These are shown in Fig. 1(a) and are due to low work function impurities on the wire surface. After a short time (one-half hour at 2000°K) these have volatilized, and a fine-grained polycrystalline emission pattern is visible [Fig. 1(b)]. At some time t_0, depending on T, the first single crystal, recognized by the symmetry of the emission pattern,[3] appears and usually grows fairly steadily in one or both directions, with an average rate R(cm/hr.) along the wire. At later times other growth centers appear, and the several crystals eventually meet. Figures 1(a–e) show various stages in the recrystallization of a 5-mil 361 wire at 2100°K.

The course of growth was recorded for each filament and plotted in a growth diagram, shown for the above wire in Fig. 2. In this diagram the positions of crystal boundaries are plotted against time, and the growth follows the irregular sloping lines. The regions to the right of these lines represent recrystallized portions of the filament, and the horizontal lines show the final boundaries between crystals.

Nineteen 218 and 361 wires were recrystallized. For each one all the data were averaged to obtain the rate of growth. Figure 3 shows $(1+\log_{10} R)$ plotted against $1000/T$. All points for wires initially 5 mil, whether slightly or deeply ground, lie close to the straight line, showing that the variation with temperature may be expressed by the equation

$$R=Ae^{-b/T}. \tag{1}$$

The slope of the line in Fig. 3 shows that the constant b is equal to $(55{,}000\pm10{,}000)$°K. Substitution in Eq. (1) of $b=55{,}000$°K and $R=0.80$ (cm/hr.) at 2000°K gives $A=7.1\times10^{-13}$ (cm/hr.).

The exponential increase with temperature is to be expected for any process in which a fairly critical amount of energy is supplied by thermal means. In the case of crystal growth this critical energy, or "activation energy," is the amount required to remove an atom from its lattice position to one of lower energy, and is roughly represented by b in Eq. (1). Actually this energy turns out to be about the same as that required to remove an electron from tungsten metal.

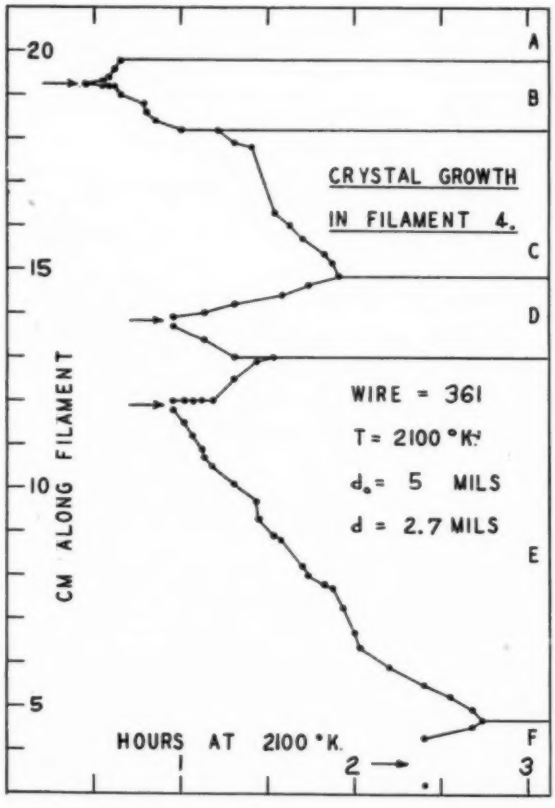


FIG. 2.

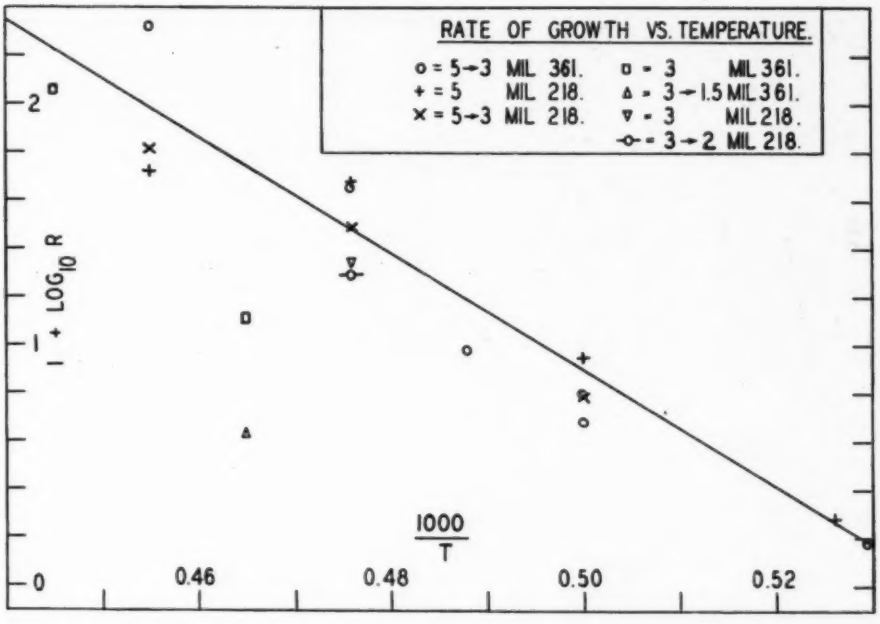


FIG. 3.

The 5-mil wires studied were recrystallized over a temperature range of 1900°K to 2200°K. These are the limits for practical recrystallization, since the time required for complete recrystallization decreases from about 100 hours to about five minutes.

IV. EFFECT OF WIRE DIAMETER

Four 218 filaments were recrystallized at 2100°K to find the effect of further drawing of the wire. The average rate of growth for wires of initial diameter 3 mils was 53 percent of that for 5-mil wires. The amount of grinding had no appreciable effect.

The further drawing must increase the mechanical strains existing in the wire, and the resultant slowing up of crystal growth is hard to explain if we use the simple picture that the fibers (i.e., crystals distorted by drawing) of the raw wire are absorbed directly into the large crystals growing along the wire. To account for the reverse effect I suggest a two-stage process which I shall call the *small grain hypothesis*. This has been previously stated by Nelson,[1] and may be illustrated by the diagram:

Fibers→small grains→large crystals.

The *small grain hypothesis* can be stated as follows:

(A) When the wire is first raised to the temperature T, the strains are quickly relieved by the breaking up of the fibers into small crystal grains; these form the polycrystalline emission pattern of Fig. 1(b).

(B) During subsequent heating some grain, presumably larger than its neighbors, begins to grow at their expense. The travel of the boundary during such growth is fairly uniform; and, after the crystal has filled the wire cross section, it expands along the wire until it meets another large crystal.

Since process (B) is relatively strain-free, the effect of drawing must be felt in (A). It is natural to assume that the grain size produced in (A) is a function of the previous strain. There is no direct evidence for the form of this relationship. However, grain growth of the type occuring in (B) is known to be more rapid for smaller grains (i.e., greater grain size contrast).[6] If we assume that grain size in (A) increases with increasing strain of the raw wire, we may then account for the slower growth in smaller wires.

V. CRYSTAL LENGTH *VS.* TEMPERATURE

The average time of appearance of growth centers, t_N, has been computed for each filament. The values for all 5-mil wires are plotted on a

[6] C. G. Smithells, *Tungsten* (Chapman and Hall, 1936), p. 88.

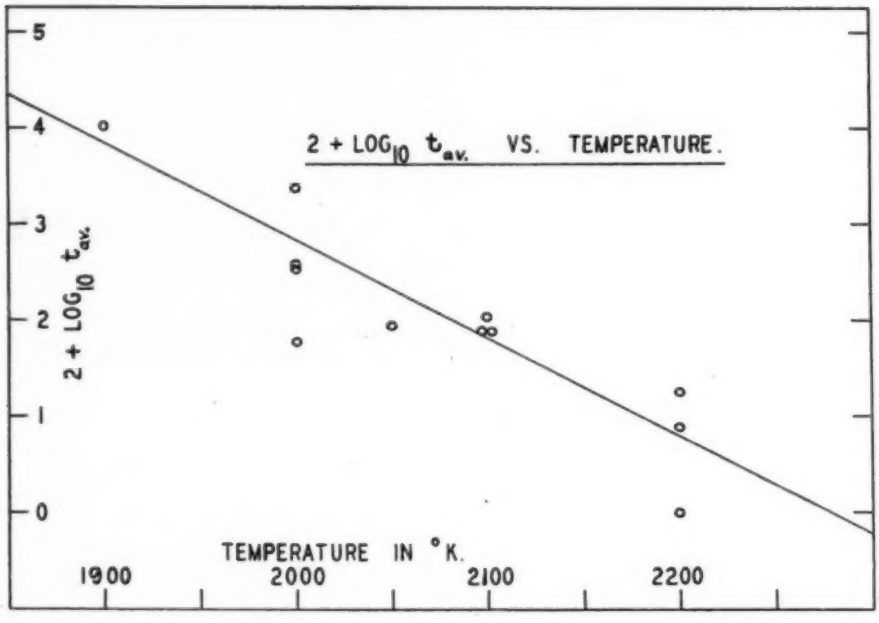


FIG. 4.

semi-logarithmic scale against temperature in Fig. 4. The straight line drawn to represent the data corresponds closely to the equation

$$t_{Ni} = Be^{+97,000/T}. \tag{2}$$

$P(T)$, the probability of appearance of a growth center, can be expressed as

$$P \sim 1/t_{Ni}. \tag{3}$$

L_{Ni}, the average length of crystal grown, depends on the ratio of rate of growth to rate of appearance of centers. Thus

$$L_{Ni} \sim Rt_{Ni}. \tag{4}$$

Substituting Eqs. (1) and (2) for R and t_{Ni} in Eq. (4) we obtain

$$L_{Ni} = Ce^{+42,000/T}. \tag{5}$$

The values of average length observed for 5-mil wires are plotted against temperature in Fig. 5. The dashed curve, corresponding to Eq. (5), is quite consistent with the data; values below the theoretical curve are to be expected at low temperatures, because (1) the study is restricted to a portion of wire about 20 centimeters long, and (2) extremely long crystals have more chance of meeting some irregularity in the wire which will shift their orientation or stop them altogether.

Table I gives values of R, L_{Ni}, and t_{Ni} for all 5-mil wires. d_0 and d are diameters before and after grinding.

VI. DISCUSSION

The crystals grown by vacuum heating are as good as those grown by the mercury-immersion method of Nichols.[3] X-ray studies of a number of wires indicate, however, that recrystallized tungsten wires will always have lineage structure. A single crystal will consist of at least six branches with a spread in orientation of 2° to 2.5°. The gradual twisting of a crystal as it grows along the wire is associated with lineage structure.

Slight differences were found between 218 and 361 wire. The rate of growth of 361 crystals

TABLE I.

Wire	d_0 (mils)	d (mils)	T (°K)	R (cm/hr.)	L_{Ni} (cm)	t_{Ni} (hr.)
218	5	4.7	1900	0.19	5.0	106
218	5	4.5	2000	0.90	4.1	23.7
218	5	3.1	2000	0.62	3.2	4.3
361	5	2.9	2000	0.48	5.8	0.6
361	5	2.9	2000	0.63	4.4	3.5
361	5	3.05	2050	0.95	1.8	0.9
218	5	5.0	2100	4.8	2.0	0.81
218	5	3.05	2100	3.1	2.0	0.78
361	5	2.7	2100	4.5	2.1	1.1
218	5	4.95	2200	5.2	0.57	0.18
218	5	3.05	2200	6.4	0.48	0.083
361	5	2.9	2200	21	0.35	0.01

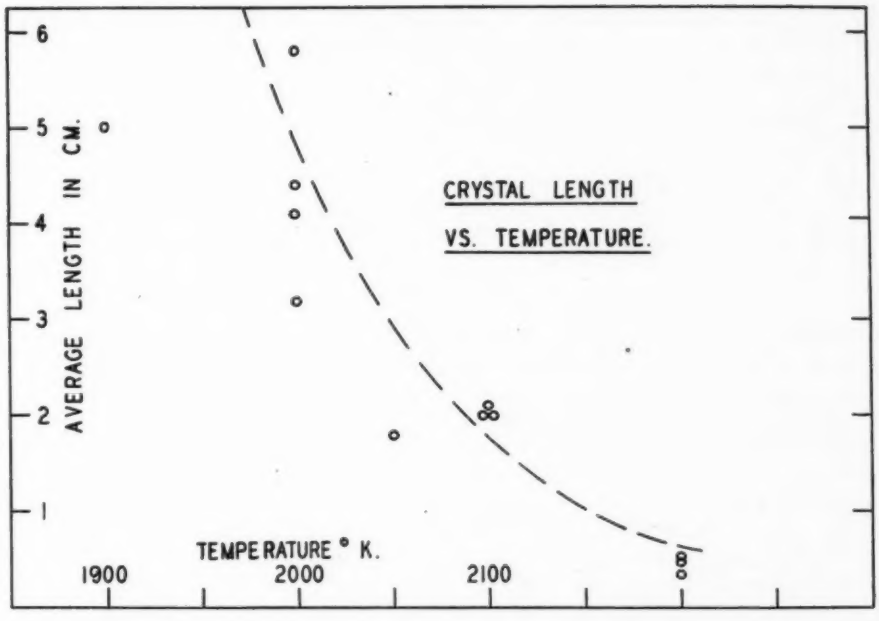


FIG. 5.

across the wire is slower, and the recrystallized wire may contain more than one crystal in a cross section.

When the wire has been heated at temperature T until it is entirely filled with large crystals, some surface imperfections may still remain. These are mostly removed by heating for 10 minutes at 2400°K. Treatments above 2800°K were not tried because the evaporation of tungsten soon spoiled the screen. A deposit of 5- or 10-atom layers reduced the secondary emission of the screens enough to destroy their usefulness.

The imperfections in the crystals are greater for lower recrystallization temperatures. For 5-mil wire, 2000°K to 2100°K is recommended as a compromise between perfection and length. For 3-mil wire, add about 100°.

I wish to acknowledge the help and advice of Professor W. B. Nottingham, who has supervised this work.

The Vibration Characteristics of Nearly-Complete, "Free-Free" Circular Rings

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(Received July 24, 1942)

The frequencies, frequency ratios, amplitudes of vibration, and mechanical constants of nearly-complete circular rings of various diameters and cross sections were measured and analyzed. The first six modes of vibration parallel to the plane of the ring, and the first five modes transverse to the plane of the ring, were obtained for several rings. The positions of the nodal points are tabulated. For the parallel vibration the frequency ratio f_n/f_1 is found to be independent of the cross section of the ring and for modes higher than the second are given accurately by the equation $f_n/f_1=0.628(n-0.200)^2$ where n is the mode. The frequencies of parallel vibration are found to be given by the equation, $f_n=(K_n/D^2)(B/m)^{\frac{1}{2}}$, where $K_1=0.285$, $K_2=0.630$, $K_n=0.1795(n-0.200)^2$ (for $n>2$), D is the mean diameter, B the bending stiffness, and m the mass per unit length. For the transverse vibration the frequency ratios depend upon the type of cross section, but are of the general form, $f_n/f_1=K^2(A/C)[n+k(A/C)]^2$, for $n>2$. The values of $K^2(A/C)$ and $k(A/C)$ are given in graphical form. A/C is the ratio of bending to twisting stiffness of the cross section of the ring. The frequency of transverse vibration is given by the equation, $f_n=[\psi_n(A/C)/D^2](A/M)^{\frac{1}{2}}$. The values of $\psi_n(A/C)$ for a wide range of A/C values are given graphically for the first six modes. The distributions of amplitude of vibration around the rings for the first three modes of both parallel and transverse vibration are shown graphically.

INTRODUCTION

ALTHOUGH much theoretical and experimental work has been done in the field of the vibration characteristics of objects of various sizes and shapes subjected to various constraints, the authors found in the literature up to the time of the beginning of this present investigation only meager information on the vibration characteristics of incomplete circular rings which are subject to no constraints. The interest of the authors in this problem was aroused during a study of the vibration characteristics of piston rings in internal combustion engines. It is believed by many that the vibration of the piston rings as they rub against the cylinder walls may cause much unwanted leakage of oil past the oil scraper rings and gases past the compression rings. A more complete knowledge of the modes and frequencies of vibration of such rings might lead to an improvement in their design and performance.

Den Hartog[1] in 1928 published a paper in which he derived by the Rayleigh-Ritz method satisfactory expressions for the natural frequencies of the first two modes of vibration, in the plane of the ring, of incomplete circular rings which subtend central angles ranging between 0 and 2π radians, and which are hinged or clamped at their ends. Using the same method, Brown[2] in 1934 derived satisfactory expressions for the natural frequencies in the first mode of vibration, transverse to their planes, of incomplete circular rings which have their ends clamped and which subtend central angles ranging from 0 to 2π radians.

Ikebe[3] has published a series of papers in which he derives by the Rayleigh-Ritz method the expressions for the natural frequencies in the first mode of vibration, in their own planes, of incomplete circular rings with free ends, and with central angles ranging from 0 to 2π radians. He also describes some experimental work performed by him which verifies reasonably well his theoretical work. In practical applications it is very important sometimes to know the frequencies of the higher modes of vibration in the plane of the ring and also transverse to the plane of the ring. To determine these characteristics the investigation reported in this paper was initiated.

[1] J. P. Den Hartog, Phil. Mag. **5**, 400 (1928).

[2] F. H. Brown, J. Frank. Inst. **218**, 41 (1934).

[3] T. Ikebe, Inst. Phys. Chem. Research, Tokyo, Sci. Paper No. 589, pp. 244–262 (Sept. 1935); and No. 796, pp. 680–712 (July, 1938).

In this paper the conventions and notations used will be the following: The coordinate system has its origin on the "neutral line" which is the locus of the center of gravity of the cross-sectional area. The x axis is taken radially inward, the y axis perpendicular to the plane of the ring, and the z axis tangent to the "neutral-line." See Fig. 1. The letters A, B, and C designate the

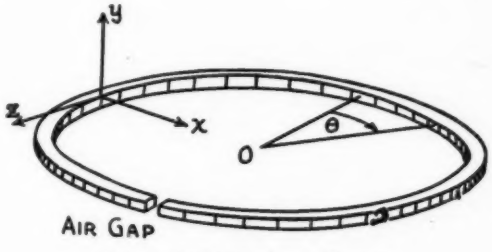

FIG. 1. System of coordinates.

bending stiffness about the x axis (i.e., EI_x), the bending stiffness about the y axis (i.e., EI_y), and the torsional stiffness about the z axis, respectively. Also,

I_x = moment of inertia of the cross section about the x axis,
I_y = moment of inertia of the cross section about the y axis,
E = Young's modulus,
G = shear modulus,
m = mass per unit length of "neutral line,"
D = diameter,
R = radius,
θ = azimuthal angle measured from a point opposite the air gap,
n = mode of vibration,
u = displacement of a point of the ring in x direction,
v = displacement of a point of the ring in y direction,
w = displacement of a point of the ring in z direction.

Vibrations in the plane of the ring shall be referred to as "parallel" and those transverse to the plane of the ring as "transverse."

EXPERIMENTAL METHODS

The rings were made from straight bars of cold rolled steel and strap iron by rolling them into smooth circles on a rolling machine. Some were painted with flat-black paint and very small dots of white paint were placed every five degrees around the circumference. The rings were supported by flexible rubber bands which were attached to wood pegs placed in convenient holes in a large wood panel.

Several methods of exciting the rings to vibrate were tried. The three most successful methods will be described in the following paragraphs. Some of the other methods tried were, first, holding a piece of solid CO_2 against the ring; and, second, placing a coil of magnet wire around the air gap of the ring and passing through the coil an alternating current from a variable-speed alternating current generator. The solid CO_2 method seemed to excite only the very high modes of vibration. In the electrical resonance method, great difficulty was found in obtaining enough power and maintaining the desired resonance frequency with the equipment available.

The first of the three successful methods of exciting the vibration consisted of placing a coil of magnet wire around the air gap of the ring and connecting the coil in series with a source of direct current, a variable speed circuit-breaker switch, and a rheostat. Difficulty was experienced in maintaining the resonance frequency, but generally the ring could be kept vibrating for several minutes at a time. Figures 2 and 3 show a ring excited in this manner vibrating in the first and second modes parallel, respectively.

The second successful method is illustrated in Fig. 4. This system operates on the same prin-

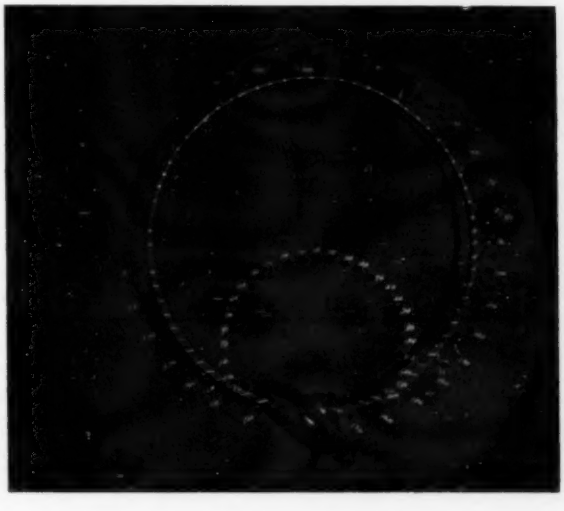

FIG. 2. First-mode parallel.

ciple as an electric doorbell. For those modes of vibration in which the free ends of the ring move in opposite directions (antisymmetric) the magnets are placed on opposite sides of the ring as shown in Fig. 4. For those modes of vibration in which the two free ends move together (symmetric) the magnets are placed on the same side. Once started in a given mode of vibration the ring continues to vibrate so until the current is turned off. One difficulty experienced in the use of this method is to get the ring started to vibrate in the desired mode.

The third successful method consisted of striking the ring with a rubber mallet while holding the ring lightly at one or more of its nodal points. This method could be used only after the exact positions of the nodal points of each of the modes of vibration had been found by exciting the ring by the other methods. This is the only method which gives a true "free" vibration and hence it was used in exciting the vibrations for all of the frequency measurements and most of the amplitude measurements.

The positions of the nodal points of the vibrating rings were determined quite accurately by rubbing a light "feeler-wire" along the ring as it vibrated. For the parallel vibrations there are no true nodal points because at the points where the radial component of displacement is zero there is considerable tangential component, and vice versa. The rings were supported by rubber bands

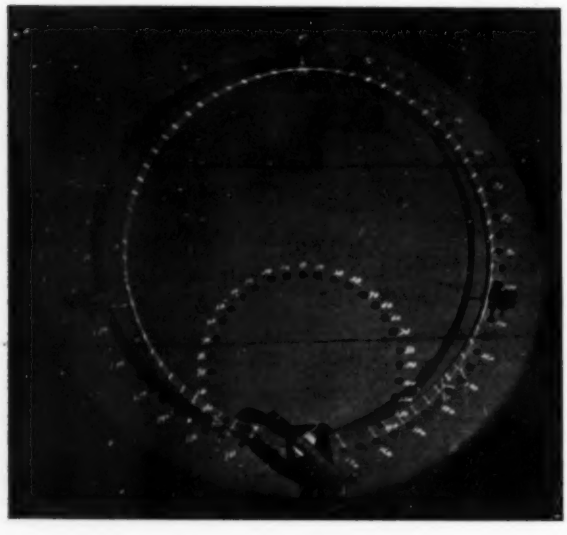

FIG. 3. Second-mode parallel.

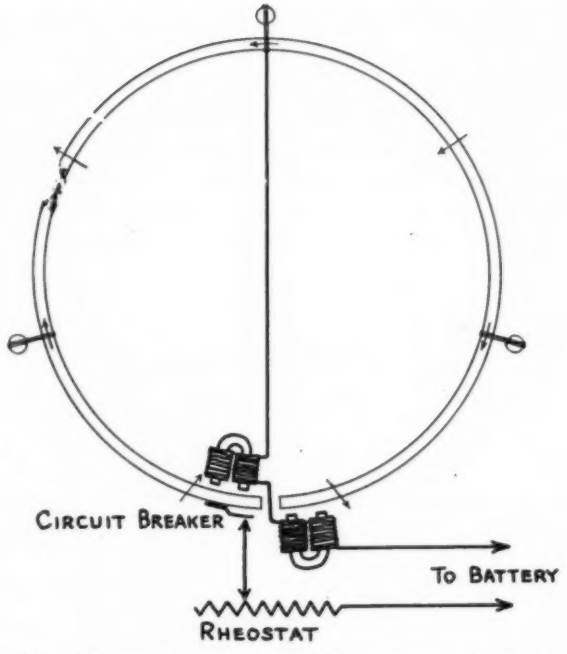

FIG. 4. Horseshoe magnets exciting ring to vibrate in second-mode parallel.

placed at the nodal points of the radial component of displacement.

At first the vibration frequencies of the rings were determined roughly by use of a General Radio Strobotac. The final measurements were made more accurately by using the Strobotac to illuminate simultaneously the vibrating ring and a vibrating standardized piano-wire reed of adjustable length. The length of the wire was adjusted until it vibrated at the same frequency as the ring, or some multiple or submultiple thereof. The frequency of the vibration was then determined by measuring the length of the wire and substituting in the frequency equation for a reed,

$$f = K/l^2. \tag{1}$$

The values of K for this particular reed were determined by operating the Strobotac directly on the 60 c.p.s. power network of the Southern Ohio Electric Company and adjusting the wire reed to the lengths necessary to make it vibrate at exact multiples or submultiples of the stroboscope light. The values of K for the various lengths of the wire are shown in Fig. 5. The decrease of K with decrease in length of the wire reed indicates that the jaws which held the wire were not perfectly rigid. The K approaches a

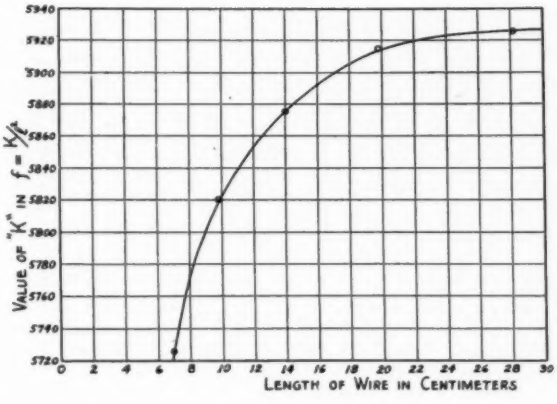

FIG. 5.

constant value, as it should theoretically, as the length of the wire is increased.

The distribution of amplitude of vibration around the ring was determined by photographing the ring as it vibrated and then again as it stood at rest. Typical photographs are shown in Figs. 2 and 3. The amplitudes of vibration at the various points were determined by measuring the elongations of the images of the little dots of white paint. In the cases of the parallel vibrations the displacements of the points on the rings were resolved into the radial and tangential components.

The elastic moduli of the ring materials were determined by measuring the deformation of the rings when known forces were applied. The deformation formulae given by Love in his book on *Mathematical Theory of Elasticity* were used. The best experimental set-up for determining the bending stiffness and the Young's modulus is illustrated in Fig. 6. In order to minimize extraneous forces in the plane of the ring, the ring was suspended in mid-air by four long threads which were attached at their upper ends to a ring of the same size. This arrangement allowed the supporting threads to remain essentially perpendicular to the plane of the ring in spite of small deformations of the ring in its own plane. Equal weights were added to the weight hangers and the change in width of the air gap was measured accurately by use of the traveling microscope. Love's formula applied to this case gives,

$$B = EI_y = \frac{F}{2w} \cdot 3\pi R^3, \tag{2}$$

and hence,

$$E = \frac{F}{2w} \cdot \frac{3\pi R^3}{I_y}, \tag{3}$$

where $F/2w$ is the ratio of the tangential force applied at the air gap to the change in width of

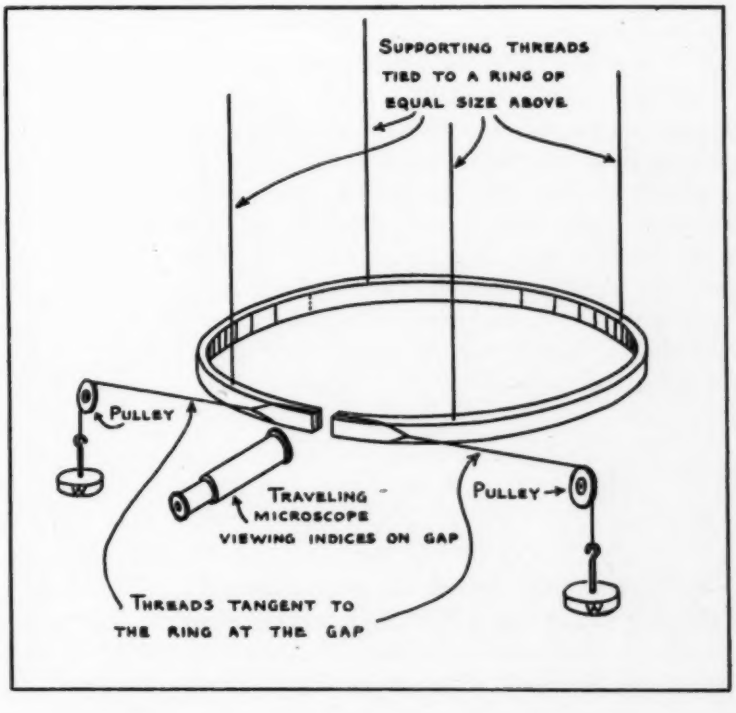

FIG. 6. Set-up for determining the bending stiffness and the Young's modulus of the rings.

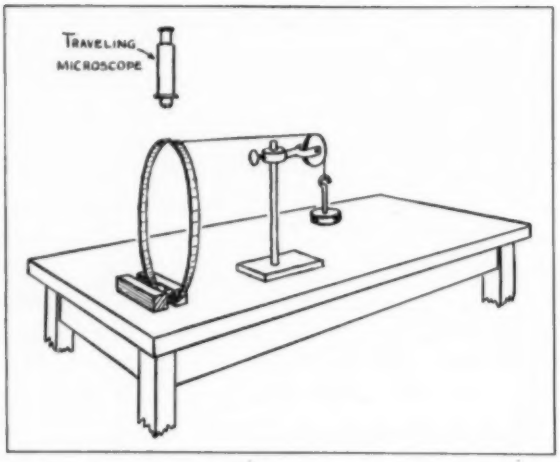

FIG. 7. Set-up for determining the torsional stiffness of the rings.

the air gap. From the value of E obtained from (3), A was calculated,

$$A = EI_z. \tag{4}$$

The Young's moduli of three of the rectangular cross section bars were determined before they were rolled into rings. This was done by statically deflecting them as "hinged-hinged" beams, and also by vibrating them as "free-free" straight bars. The shear moduli of the same pieces were determined by using them as the torsion elements of a torsion pendulum.

The experimental arrangement for determining the torsional stiffness and the shear modulus is illustrated in Fig. 7. The ring was clamped firmly by hard wood blocks at the point opposite the air gap. A known force was applied at one of the free ends of the ring by a thread perpendicular to the plane of the ring. The deflection v of the one free end with respect to the other was measured accurately by means of the traveling microscope shown. For this case Love's equation, when solved for the torsional stiffness, gives,

$$C = \frac{\frac{3}{2}\pi FR^3}{v - \frac{\pi}{2}\frac{FR^3}{A}}, \tag{5}$$

where F is the force applied, v is the displacement of the free end in the y direction, and the other terms have their usual significance. To determine C from this equation, A must have been previously determined in the manner described above. For rings of circular cross section the shear modulus is obtained by dividing C by the polar moment of inertia of the cross section. For rings of rectangular cross section the shear modulus may be obtained from the relation,[4]

$$C = \beta bc^3 G, \tag{6}$$

where b is the major and c the minor dimension of the cross section, and β is a parameter, first evaluated by St. Venant,[5] which depends upon the b/c ratio.

After ten rings had been made and the results

TABLE I. Angular positions of the nodal points of the radial component of the parallel vibration.

Mode of vibration	Positions of the nodal points						
1	—	—	−30°	—	30°	—	—
2	—	—	−105°	0°	105°	—	—
3	—	−135°	−50°	—	50°	135°	—
4	—	−147°	−78.5°	0°	78.5°	147°	—
5	−153°	−96.5°	−32°	—	32°	96.5°	153°
6	−159°	−110°	−56°	0°	56°	110°	159°

TABLE II. Angular positions of the nodal points of the transverse vibration.

Mode of vibration	Positions of the nodal points						
1	—	—	−107°	0°	107°	—	—
2	—	−142.5°	−50°	—	50°	142.5°	—
3	—	−153°	−82.5°	0°	82.5°	153°	—
4	−160°	−102.5°	−33°	—	33°	102.5°	160°
5	−162°	−113°	−56.5°	0°	56.5°	113°	162°

TABLE III.

Mode	Vibrator*	Positions of nodal points Fraction of length of bar						
1	*A*			0.222		0.778		
	B			.415		.585		
	C			.200	0.500	.800		
2	*A*			.133	.500	.867		
	B			.205	.500	.795		
	C		0.099	.359		.641	0.901	
3	*A*		.093	.353		.647	.907	
	B		.120	.373		.627	.880	
	C		.069	.268	.500	.732	.931	
4	*A*		.076	.277	.500	.723	.924	
	B		.086	.279	.500	.721	.914	
	C	0.050	.211	.404		.596	.789	0.950
5	*A*	.060	.223	.407		.593	.777	.940
	B	.069	.228	.410		.590	.772	.931
	C	.044	.183	.341	.500	.659	.817	.956
6	*A*	.0475	.191	.346	.500	.654	.809	.9525
	B	.052	.190	.342	.500	.658	.810	.948

* *A* = straight bar; *B* = ring parallel; *C* = ring transverse.

[4] S. Timoshenko, *Strength of Materials*, second edition (Van Nostrand, 1940).

[5] Saint Venant, *Mémoires des Savants étranges*, Table 14 (1855).

from them compiled it was found that the accuracy of the results was not quite sufficient to prove definitely some of the relationships indicated by them. Consequently three more rings whose A/C ratios had certain desired values were made and ground to give accurate cross sections. Their moduli were measured accurately while they were still in the form of straight bars. These rings are indicated in Tables IV and V by double stars.

RESULTS

The angular positions of the nodal points for the radial components of the first six modes of the parallel vibration are given in Table I. The angles are measured from the point diametrically opposite the center of the air gap. Table II shows the angular positions of the nodal points for the first five modes of transverse vibration. Table III shows the positions of the nodal points, expressed in terms of the fraction of the length of the bar from a free end, for the three cases: (a) transverse vibration of a straight bar, (b) parallel vibration of a nearly-complete circular ring, and (c) transverse vibration of a nearly-complete circular ring. It is seen that the positions of the nodal points for the higher modes of vibration of the rings approach those of a straight bar vibrating in a comparable mode.

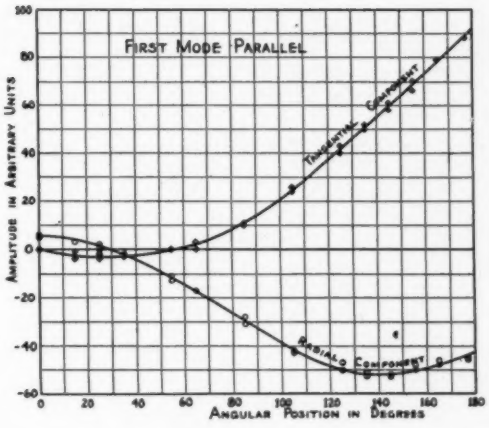

FIG. 9.

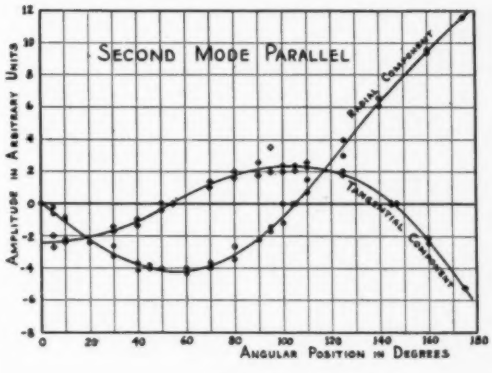

FIG. 10.

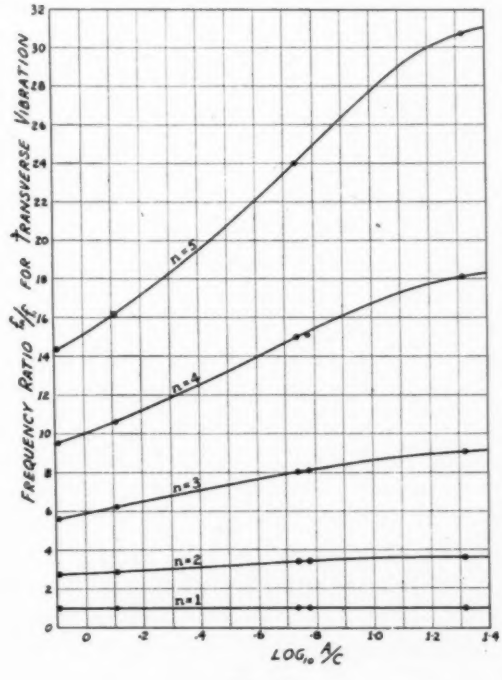

FIG. 8.

The frequencies of vibration of the various rings vibrating in different modes are given in Table IV. The four rings of square cross section were made from the same piece of cold rolled steel and hence they had nearly identical cross sections. The three rings marked "Rect.$_4$" were made from the same piece of strap iron and therefore had nearly identical cross sections. Table V gives the ratios of the frequencies in the various modes to the frequency of the first mode, f_n/f_1. It is evident that within the limits of experimental error the frequency ratios for the parallel type of vibration is independent of the type of cross section. This is to be expected since the parallel vibration involves only simple bending of the bar about the y axis. However, for the transverse type of vibration the frequency ratios depend upon the type of cross section. This is to be expected since the transverse vibration involves

TABLE IV. Observed frequencies of vibration.

(Frequency c.p.s.)

Diam. (cm)	Type of cross section	A/C ratio	Mode parallel 1	2	3	4	5	6	Mode transverse 1	2	3	4	5
51.9**	Rect.$_1$	0.812	19.60						9.62	26.25	54.2	91.5	138.2
49.7*	Round (Approx.)	1.28	9.30	20.52	45.75	83.3	134.5	197.2	11.27	32.16	70.4	119.8	182.0
9.70	square	1.60	209.5						238				
14.00	"	1.57	100.0	220.5					113	320			
21.15	"	1.50	44.4	97.1	218.0				49.7	147			
32.0	"	1.50	19.8	43.7	97.1	178.1			22.6	66.0	144		
55.9**	Rect.$_2$	5.48	6.40						10.77	36.6	86.8	161.8	259
32.4*	Rect.$_3$ (Approx.)	6.00	19.17	42.1	96.0	175.3			32.5	111.2	264	492	
22.75	Rect.$_4$	12.2	25.4	55.1	123.0				45.6	162			
30.7	"	12.0	13.96	30.8	68.3	126.4			25.6	93.0	230		
45.8	"	11.8	6.32	14.05	31.35	56.9	91.5	133.5	11.70	41.7	105.0	209	
56.8**	Rect.$_5$ (Approx.)	20.7							7.78	28.1	70.9	141.0	239.5
49.3	Rect.$_6$	24.0	5.45	12.13	27.15	50.4	79.9	117.7	10.20	37.5	95.3	187.6	

* Fairly accurate cross section.
** Accurately machined, best rings.

TABLE V. Frequency ratios.

Frequency ratio f_n/f_1

Diam. (cm)	Type of cross section	A/C ratio	Mode parallel 1	2	3	4	5	6	Mode transverse 1	2	3	4	5
51.9**	Rect.$_1$	0.812	1						1	2.73	5.63	9.50	14.36
49.7*	Round (Approx.)	1.28	1	2.21	4.87	8.96	14.45	21.2	1	2.85	6.24	10.63	16.15
9.70	square	1.60	1						1				
14.00	"	1.57	1	2.205					1	2.83			
21.15	"	1.50	1	2.19	4.91				1	2.95			
32.0	"	1.50	1	2.21	4.90	9.00			1	2.92	6.37	11.1	
55.9**	Rect.$_2$	5.48	1						1	3.40	8.06	15.0	24.0
32.4*	Rect.$_3$ (Approx.)	6.00	1	2.20	5.01	9.15			1	3.42	8.12	15.1	
22.75	Rect.$_4$	12.2	1	2.17	4.84				1	3.55			
30.7	"	12.0	1	2.21	4.89	9.06			1	3.63	8.98		
45.8	"	11.8	1	2.22	4.96	9.00	14.46	21.2	1	3.56	8.98	17.9	
56.8**	Rect.$_5$ (Approx.)	20.7							1	3.61	9.11	18.13	30.7
49.3	Rect.$_6$	24.0	1	2.23	4.98	9.24	14.66	21.2	1	3.67	9.34	18.4	
		Average	1	2.205	4.92	9.07	14.5	21.2					

* Fairly accurate cross section.
** Accurately machined, best rings.

twisting as well as bending of the bar, and hence there should be a definite relationship between the frequency ratios and the ratio of the bending stiffness to torsional stiffness of the bar. This relationship, taken from the experimental data, is shown graphically in Fig. 8.

The distribution of amplitude around the ring for the first three modes of parallel and transverse vibration are shown in Figs. 9, 10, 11, and 12. In the first-mode parallel (Fig. 9) it is seen that the maximum radial displacement occurs at ±140°, and this maximum displacement is about ten times that at the 0° position. The tangential displacement vanishes at 0° and ±55°, with the maximum at the free ends (±178°) being about thirty times that at ±25°. The tangential amplitude at ±178° is about 1.73 times the maximum radial amplitude at ±140°. These experimental results agree almost perfectly with the theoretical values derived by Ikebe.[6]

In the second-mode parallel (Fig. 10) the amplitude of the radial component at the free ends (±178°) is about 2.8 times that at ±55°.

[6] T. Ikebe, reference 3, No. 3.

The tangential component vanishes at $\pm 53°$ and $\pm 147°$. The ratio of the tangential component at the free ends to that at $\pm 105°$ is about 2.5. The ratio of the tangential to the radial displacement at the free ends is 0.5 as compared to 1.73 for the first mode.

For the third-mode parallel (Fig. 11) the displacements were so small that it was not possible to measure them accurately from the photographs. The maxima of the radial components of displacement which occur at $0°$, $\pm 90°$, and at the free ends, are in the ratio 0.35/0.27/1.00 as compared to 0.71/0.66/1.00 for the corresponding vibration of a straight bar. The ratio of the tangential to the radial component at the free ends is roughly 0.075. In general, for the modes of parallel vibration higher than the third the tangential component of vibration is quite small in comparison to the radial component, but it never vanishes as completely as it does for a straight bar.

Figure 12 shows the relative displacements in the first three modes of transverse vibration. For comparison, the ratios of the transverse displacements at the antinodal points of vibrating straight bars and nearly-complete circular rings are given in Table VI. It is important to notice the nth mode of transverse vibration of the rings corresponds in form to the $(n+1)$th mode of the other two cases. In all modes, the form of the transverse vibration of the ring approaches that of the straight bar more nearly than that of the parallel vibration of the ring.

The values of Young's modulus for the various rings, as determined by the method illustrated in Fig. 6, ranged from 18.8×10^{11} up to 21.1×10^{11} dynes per cm^2. The average was 20.2×10^{11}. The shear moduli, as determined by the method illustrated in Fig. 7, ranged from 6.43×10^{11} to 8.07×10^{11} dynes per cm^2. The average was 7.43×10^{11}. This is too low.

TABLE VI. Ratios of the transverse displacements at the antinodes of vibrating straight bars and incomplete circular rings. (The amplitude of the free ends is taken as unity.)

Mode	Straight bar	Incomplete circular ring, parallel vibration	Incomplete circular ring, transverse vibration
1	1.00/0.60	1.00/0.10	1.00/0.28
2	1.00/0.65	1.00/0.37	1.00/0.45/0.50
3	1.00/0.66/0.71	1.00/0.27/0.35	1.00/0.62/0.55
4	1.00/0.64/0.70		

In nearly all the cases the force-displacement ratios were determined with such accuracy that the variation of individual values from the mean for a given ring was within one percent of the mean, yet the elastic moduli as determined by Love's formulae for the different rings made from the same original straight bar of steel varied as much as four percent from the mean for the Young's modulus and 13 percent from the mean for the shear modulus. In one case in which the elastic moduli of the steel were determined before the straight bar was rolled into the circular ring the values obtained by the different methods could be compared. By static deflection the Young's modulus was 20.55×10^{11}, by vibrating it as a "free-free" straight bar it was 20.50×10^{11}, and by bending the ring as in Fig. 6 it was 19.4×10^{11}. The individual readings of each test agreed within one-half percent so it may be concluded that the relationship given in Love's book is not sufficiently accurate. The "cold working" of the metal during the rolling process should

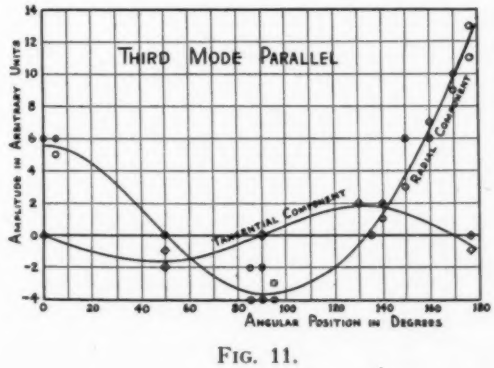

FIG. 11.

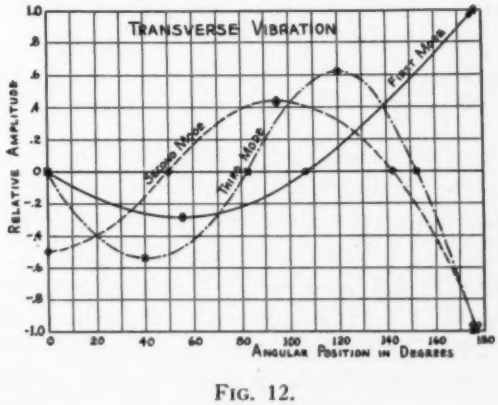

FIG. 12.

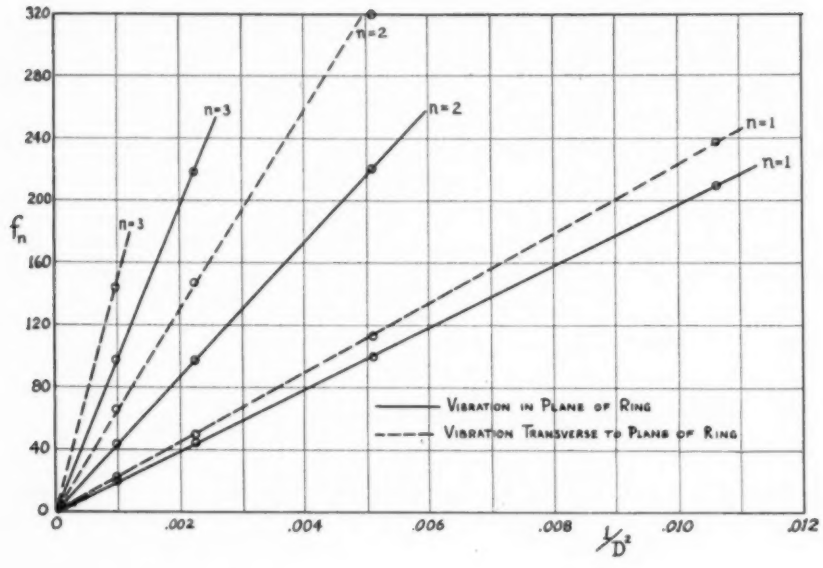

FIG. 13.

have increased rather than decreased the Young's modulus. The shear modulus of the same straight bar of steel was determined by using it as the torsion element of a torsion pendulum. The value obtained was 7.93×10^{11} dynes per cm^2 which is about right for cold rolled steel. Again, it may be inferred that the expression given in Love's book for the transverse deflection of a circularly-curved bar is not sufficiently accurate, especially for the rings of smaller diameter.

The values of the stiffness constants, A, B, and C, which were used in the final calculation of the frequency constants from the experimental data, were obtained by using for Young's modulus the value 20.5×10^{11} dynes per cm^2, and for the shear modulus, the value 8.00×10^{11} dynes per cm^2.

CONCLUSIONS

The expression for the frequency of vibration of any kind of bar must be of the general form,

$$f=\frac{\text{constant}}{(\text{linear dimension})^2}\left(\frac{\text{stiffness factor}}{\text{linear density}}\right)^{\frac{1}{2}}. \quad (7)$$

The general validity of this equation for nearly-complete circular rings is shown by the experimental results put up in the form of Figs. 13 and 14. Figure 13 shows the frequencies of vibration in the different modes of both parallel and transverse vibration of a family of four rings of identical cross sections but different diameters. Figure 14 shows the same for a similar family of three rings of rectangular cross section. The fact that all the points for corresponding modes of vibration lie on straight lines indicates that the frequency varies accurately as the inverse square of the mean diameter of the ring.

For vibrations involving pure bending the constant in (7) will depend only upon the mode of vibration. This condition holds true for the parallel vibrations of rings and therefore the parallel vibration frequency may be expressed in the form,

$$f_n=\frac{K_n}{D^2}\left(\frac{B}{m}\right)^{\frac{1}{2}}. \quad (8)$$

For straight bars, K_n varies as $(n+\frac{1}{2})^2$, and since $K_n/K_1=f_n/f_1$, the frequency ratio f_n/f_1 also

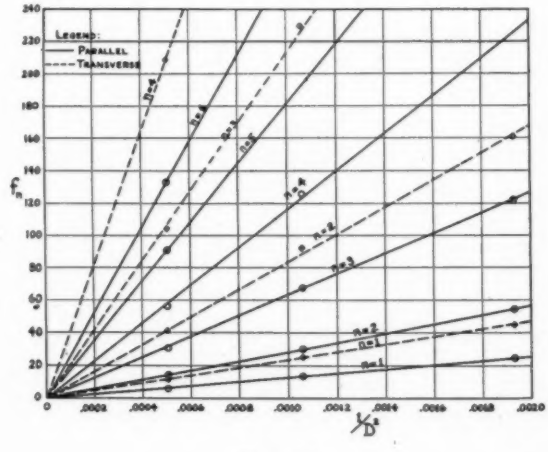

FIG. 14.

varies as $(n+\frac{1}{2})^2$. Therefore $(f_n/f_1)^{\frac{1}{2}}$ plotted against n should give a straight line intercepting the n axis at $n=-\frac{1}{2}$. This is shown in Fig. 15. In the same figure the same variables are plotted for the parallel vibration of incomplete circular rings. It is seen that for $n>2$ there is also a linear relationship between $(f_n/f_1)^{\frac{1}{2}}$ and n for the case of the rings. The equation of the line is found to be $(f_n/f_1)^{\frac{1}{2}}=0.792(n-0.200)$, whence,

$$f_n/f_1=0.628(n-0.200)^2, \qquad \text{for} \qquad n>2. \quad (9)$$

The accuracy of this relationship is shown in Table VII. Its accuracy appears to be great enough that it may be successfully used in predicting the frequency ratios of much higher modes of vibration.

The values of K_n may be calculated from the experimental data. By using Eq. (9) the values of K_n are found to be expressed by the equation,

$$K_n=0.1795(n-0.200)^2, \qquad (10)$$

when c.g.s. units are used. Table VII gives the observed and the calculated values by Eq. (10) of K_n.

TABLE VII. Frequency ratios and constants *vs.* mode of parallel vibration.

	f_n/f_1		K_n	
Mode	Calculated by (9)	Observed	Calculated by (10)	Observed
1	0.402	1.00	0.115	0.285
2	2.04	2.205	0.581	0.630
3	4.93	4.92	1.41	1.40
4	9.08	9.07	2.59	2.59
5	14.5	14.5	4.13	4.13
6	21.2	21.2	6.04	6.04

TABLE VIII. Calculated and observed values of f_n/f_1 for transverse vibration of rings.

A/C	$k(A/C)$	$K^2(A/C)$	n	f_n/f_1 (calc.)	f_n/f_1 (obs.)
			5	14.37	14.36
0.812	0.340	0.504	4	9.50	9.50
			3	5.62	5.63
			5	16.20	16.15
1.28	0.285	0.580	4	10.66	10.63
			3	6.26	6.24
			5	24.05	24.0
5.48	−0.240	1.06	4	15.00	15.0
			3	8.07	8.06
			5	30.7	30.7
20.7	−0.740	1.69	4	17.97	18.13
			3	8.63	9.11

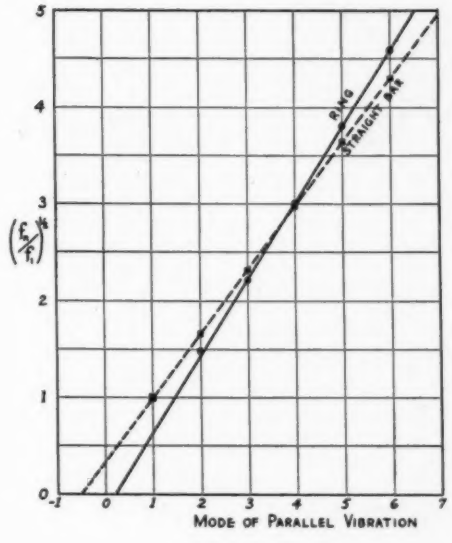

FIG. 15.

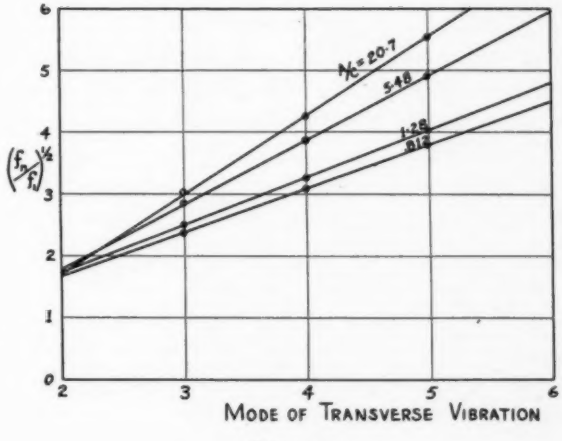

FIG. 16.

For the transverse vibrations, in which twisting as well as bending is involved, the "constant" of Eq. (7), and consequently the frequency ratios, must depend upon the ratio of the bending stiffness about the x axis to the torsional stiffness. Figure 16 shows that for $n>2$ there is a linear relationship between $(f_n/f_1)^{\frac{1}{2}}$ and n. The greater the A/C ratio the more rapidly $(f_n/f_1)^{\frac{1}{2}}$ increases with n. The family of straight lines has the general formula,

$$\left(\frac{f_n}{f_1}\right)^{\frac{1}{2}}=F\left(\frac{A}{C},n\right)=K\left(\frac{A}{C}\right)\cdot\left[n+k\left(\frac{A}{C}\right)\right]. \quad (11)$$

The values of the functions $K(A/C)$ and $k(A/C)$ obtained from the experimental data are shown

in Fig. 17. The frequency ratios may be calculated directly from the expression,

$$\frac{f_n}{f_1}=F^2\left(\frac{A}{C},n\right)=K^2\left(\frac{A}{C}\right)\cdot\left[n+k\left(\frac{A}{C}\right)\right]^2. \quad (12)$$

The values of $K^2(A/C)$ may be taken directly from Fig. 17. Table VIII compares the observed values of f_n/f_1 from the rings of accurate cross section with those calculated by use of Eq. (12). This comparison shows that the curves of Fig. 17 and Eq. (12) may be used with confidence for values of n greater than 2 or 3. The greater the value of A/C the greater the value of n at which the $(f_n/f_1)^{\frac{1}{2}}$ *vs.* n curve approaches linearity.

For the transverse vibrations Eq. (7) may be written in the form,

$$f_n=\frac{\psi_n(A/C)}{D^2}\left(\frac{A}{m}\right)^{\frac{1}{2}}. \quad (13)$$

The values of ψ_n for the first five modes of transverse vibration, determined from the experimental results, are shown in Fig. 18.

In the work reported in this paper great effort was made to keep errors of measurement smaller than one-half percent. In spite of this some of the data are not self-consistent to this accuracy. These inconsistencies are believed to be due mainly to variations in the cross section and metallurgical structure of the rings which were beyond control with the facilities available. Nevertheless it is believed that the final averaged

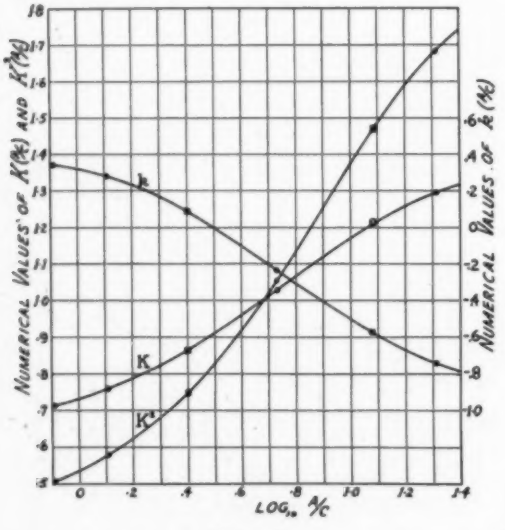

FIG. 17.

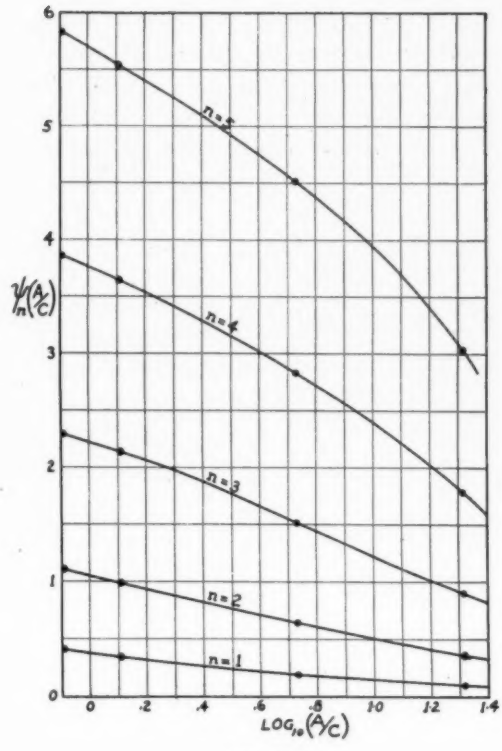

FIG. 18.

curves are accurate to within one percent for the most part and certainly not more than four percent at the worst points.

Ikebe's theoretically derived equations give for the frequency constant K_1 of the first mode of parallel vibration of a ring having a 4° air gap the value 0.275. The best and average value obtained from the experimental results is 0.285 with the values ranging from 0.271 to 0.294. The accurately machined rings whose moduli had been measured while in straight bar form, gave a value for K_1 of precisely 0.285. These results infer that Ikebe's theory is in error by about four percent.

This investigation immediately suggests a similar set of measurements on circularly curved bars having central angles ranging between 0° and 360°. Work on this problem has been started. It is also suggested that similar measurements could be made for "hinged-hinged" and "clamped-clamped" circularly curved bars to supplement the work of Den Hartog[1] and of Brown.[2]

The authors wish to express their appreciation to Mr. H. A. Gehres and Mr. Ralph Boyer of the Cooper-Bessemer Corporation for their interest and help in this investigation.